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Supporting Information

Nickel-Catalyzed Regioselective C–H Halogenation of Electron-Deficient Arenes

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1.General information

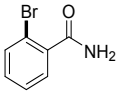
All compounds are characterized by ^{1}H NMR, ^{13}C NMR and MS. Analytical thin-layer chromatography is performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm.GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413:30 m × 320 μm × 0.25 μm, H, FID detection). GC-MS data was recorded on a 5975C Mass Selective Detector,coupled with a 7890A Gas Chromatograph (Agilent Technologies).

2.General procedure

General procedure for the synthesis of mono-bromination product: To a mixture of benzamide (0.5 mmol) **1a**, $Ni(OAc)_2$ (15%mmol), $AgSbF_6$ (0.2 equiv), TfOH (0.5 equiv), and DCE (1.5ml) in a reaction tube was added N-bromosuccinimide (NBS) (1.5 equiv.). The reaction mixture was stirred at 80°C for 12h. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired products **3a**.

General procedure for the synthesis of di-bromination product: To a mixture of benzamide (0.5 mmol) **1a**, $Ni(OAc)_2$ (15%mmol), $AgSbF_6$ (0.2 equiv), TfOH (0.5 equiv), and DCE (1.5ml) in a reaction tube was added N-bromosuccinimide (NBS) (2.5 equiv.). The reaction mixture was stirred at 80°C for 36h. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired products **5a**.

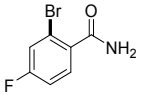
3.Characterization data



Formula: C_7H_6BrNO

Mass: 199

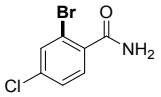
2-bromobenzamide (3a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3a** as white solid (81.59mg, 82%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.63 (m, 2H), 7.46 – 7.41 (m, 1H), 7.38 – 7.33 (m, 1H), 6.16 (s, 1H), 6.02 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.1, 135.6, 132.6, 130.7, 129.0, 126.6, 118.2. GC-MS (EI) *m/z*: 199.



Formula: C_7H_5BrFNO

Mass: 217

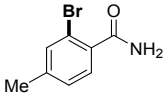
2-bromo-4-fluorobenzamide (3b): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3b** as white solid (85.72mg, 79%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.37 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.16 (s, 1H), 6.03 (s, 1H). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.37 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.14 (s, 1H), 6.04 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.1, 163.2, 131.7, 130.9, 120.1, 119.9, 114.1, 114.0. GC-MS (EI) *m/z*: 217.



Formula: $C_7H_5BrClNO$

Mass: 233

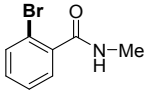
2-bromo-4-chlorobenzamide (3c): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3c** as white solid (89.71mg, 77%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.58 (m, 2H), 7.38 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.15 (s, 1H), 6.00 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.2, 136.2, 133.9, 132.3, 130.1, 127.0, 118.8. GC-MS (EI) *m/z*: 233.



Formula: C_8H_8BrNO

Mass: 213

2-bromo-4-methylbenzamide (3d): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3d** as white solid (72.42mg, 68%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.72 (s, 1H), 7.43 (s, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.14 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.5, 140.2, 135.8, 132.4, 127.9, 127.5, 118.0, 19.8. GC-MS (EI) *m/z*: 213.

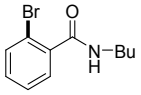


Formula: C_8H_8BrNO

Mass: 213

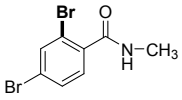
2-bromo-N-methylbenzamide (3e): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3e** as white solid (77.75mg, 73%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.33 – 7.29 (m, 1H), 6.07 (s,

1H), 3.07 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.3, 136.9, 132.4, 130.2, 128.6, 126.6, 118.3, 25.8. GC-MS (EI) *m/z*: 213.



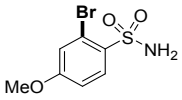
Formula: $C_{11}H_{14}BrNO$
Mass: 255

2-bromo-N-(tert-butyl)benzamide (3f): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3f** as white solid (89.25mg, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.35 – 7.31 (m, 1H), 7.26 – 7.21 (m, 1H), 5.73 (s, 1H), 1.48 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.0, 138.1, 132.2, 130.8, 129.9, 128.3, 126.5, 51.3, 27.8. GC-MS (EI) *m/z*: 255.



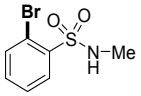
Formula: $C_8H_7Br_2NO$
Mass: 293

2,4-dibromo-N-methylbenzamide (3g): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3g** as white solid (92.30mg, 63%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 1.8 Hz, 1H), 7.53 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 6.13 (s, 1H), 3.05 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.3, 135.7, 134.8, 133.0, 129.8, 123.5, 119.0, 25.8. GC-MS (EI) *m/z*: 293.



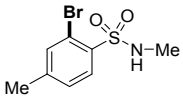
Formula: $C_7H_8BrNO_3S$
Mass: 265

2-bromo-4-methoxybenzenesulfonamide (3h): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3h** as white solid (91.43mg, 69%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 2.3 Hz, 1H), 7.87 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.8, 133.8, 130.9, 126.6, 111.4, 110.4, 55.7. GC-MS (EI) *m/z*: 265.



Formula: $C_7H_8BrN_2OS$
Mass: 249

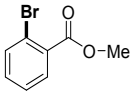
2-bromo-N-methylbenzenesulfonamide (3i): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3i** as white solid (93.34mg, 75%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.79 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.60 – 7.29 (m, 3H), 2.66 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.6, 134.1, 132.8, 131.1, 126.9, 118.6, 28.3. GC-MS (EI) *m/z*: 249.



Formula: $C_8H_{10}BrNO_2S$
Mass: 263

2-bromo-N,4-dimethylbenzenesulfonamide (3j): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3j** as white solid (93.37mg, 71%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.1 Hz,

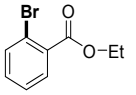
1H), 7.56 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.28 – 7.26 (m, 1H), 2.60 (d, *J* = 5.4 Hz, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.1, 134.5, 133.6, 131.1, 127.5, 118.4, 28.3, 20.1. GC-MS (EI) *m/z*: 263.



Formula: $C_8H_7BrO_2$

Mass: 214

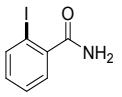
methyl 2-bromobenzoate (3k): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3k** as white solid (81.32mg, 76%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38 – 7.27 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.6, 133.3, 131.6, 131.2, 130.3, 126.2, 120.6, 51.5. GC-MS (EI) *m/z*: 214.



Formula: $C_9H_9BrO_2$

Mass: 228

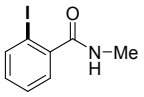
ethyl 2-bromobenzoate (3l): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3l** as white solid (74.90mg, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.40 – 7.28 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.3, 133.3, 131.6, 131.4, 130.2, 126.2, 120.5, 60.6, 13.2. GC-MS (EI) *m/z*: 228.



Formula: C_7H_6INO

Mass: 247

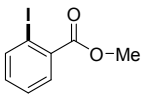
2-iodobenzamide (4a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **4a** as white solid (100.04mg, 81%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.80 (s, 1H), 7.49 (s, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.33 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.13 (td, *J* = 7.6, 1.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.1, 142.6, 138.6, 130.0, 127.4, 127.2, 92.6. GC-MS (EI) *m/z*: 247.



Formula: C_8H_8INO

Mass: 261

2-iodo-N-methylbenzamide (4b): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **4b** as white solid (99.18mg, 76%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.77 (m, 1H), 7.48 – 7.32 (m, 2H), 7.10 (m, 1H), 5.77 (s, 1H), 3.03 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.1, 141.4, 138.9, 130.1, 127.2, 126.8, 91.5, 25.8. GC-MS (EI) *m/z*: 261.

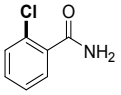


Formula: $C_8H_7IO_2$

Mass: 262

methyl 2-iodobenzoate (4c): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **4c** as white

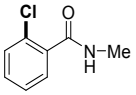
solid (100.87mg, 77%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.78 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.38 (td, *J* = 7.6, 1.1 Hz, 1H), 7.13 (td, *J* = 7.6, 1.8 Hz, 1H), 3.92 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.9, 140.3, 134.1, 131.7, 130.0, 126.9, 93.1, 51.5. GC-MS (EI) *m/z*: 262.



Formula: C_7H_6ClNO

Mass: 155

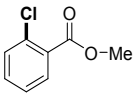
2-chlorobenzamide (4d): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **4d** as white solid (54.25mg, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.74 (m, 1H), 7.57 – 7.32 (m, 3H), 6.69 (s, 1H), 6.46 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.5, 132.9, 130.8, 129.9, 129.6, 129.4, 126.2. GC-MS (EI) *m/z*: 155.



Formula: C_8H_8ClNO

Mass: 169

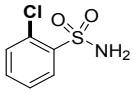
2-chloro-N-methylbenzamide (4e): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **4e** as white solid (55.77mg, 66%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.41 – 7.32 (m, 3H), 6.24 (s, 1H), 3.03 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.2, 134.1, 130.3, 129.6, 129.2, 128.9, 126.1, 25.8. GC-MS (EI) *m/z*: 169.



Formula: $C_8H_7ClO_2$

Mass: 170

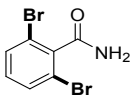
methyl 2-chlorobenzoate (4f): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **4f** as white solid (58.65mg, 69%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (m, 2H), 7.30 (td, *J* = 7.5, 1.4 Hz, 1H), 3.93 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.1, 132.7, 131.5, 130.4, 130.0, 129.1, 125.6, 51.4. GC-MS (EI) *m/z*: 170.



Formula: $C_6H_6ClNO_2S$

Mass: 191

2-chlorobenzenesulfonamide (4g): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **4g** as white solid (67.81mg, 71%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.97 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.65 – 7.56 (m, 4H), 7.51 (td, *J* = 7.6, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 140.5, 132.9, 131.0, 129.8, 128.4, 126.9. GC-MS (EI) *m/z*: 191.

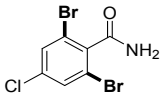


Formula: $C_7H_5Br_2NO$

Mass: 279

2,6-dibromobenzamide (5a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5a** as white solid (104.63mg, 75%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.1 Hz, 2H),

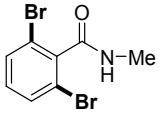
7.13 (t, *J* = 8.0 Hz, 1H), 5.94 (s, 1H), 5.73 (s, 1H).^{13}C NMR (126 MHz, DMSO-d6) δ 166.3, 135.5, 132.5, 128.9, 127.8. GC-MS (EI) *m/z*: 279.



Formula: $C_7H_4Br_2ClNO$

Mass: 312

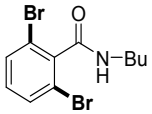
2,6-dibromo-4-chlorobenzamide (5b): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5b** as white solid (112.32mg,72%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (s, 2H), 6.02 (s, 1H), 5.77 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.2, 136.8, 135.3, 130.7, 119.3. GC-MS (EI) *m/z*: 312.



Formula: $C_8H_7Br_2NO$

Mass: 293

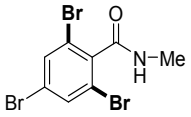
2,6-dibromo-N-methylbenzamide (5c): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5c** as white solid (108.41mg, 74%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 8.1 Hz, 1H), 5.79 (s, 1H), 3.09 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.1, 139.0, 130.8, 130.1, 119.5, 25.7. GC-MS (EI) *m/z*: 293.



Formula: $C_{11}H_{13}Br_2NO$

Mass: 334

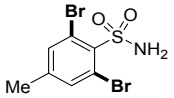
2,6-dibromo-N-(tert-butyl)benzamide (5d): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5d** as white solid (115. 23mg, 69%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 5.48 (s, 1H), 1.49 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.2, 139.4, 130.8, 130.0, 119.5, 51.6, 27.7. GC-MS (EI) *m/z*: 344.



Formula: $C_8H_6Br_3NO$

Mass: 371

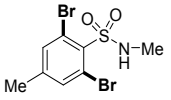
2,4,6-tribromo-N-methylbenzamide (5e): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5e** as white solid (105.74mg, 57%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (s, 2H), 5.83 (s, 1H), 3.08 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.4, 137.9, 133.3, 122.8, 120.0, 25.7. GC-MS (EI) *m/z*: 371.



Formula: $C_7H_7Br_2NO_2S$

Mass: 329

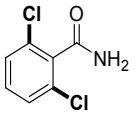
2,6-dibromo-4-methylbenzenesulfonamide (5f): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5f** as white solid (100.35mg, 61%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.61 (s, 1H), 5.18 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.8, 137.9, 135.5, 132.3, 21.8. GC-MS (EI) *m/z*: 329.



Formula: $C_8H_9Br_2NO_2S$

Mass: 343

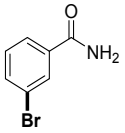
2,6-dibromo-N,4-dimethylbenzenesulfonamide (5g): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5g** as white solid (94.33mg, 55%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 7.60 (s, 1H), 5.03 (s, 1H), 2.64 (d, *J* = 5.4 Hz, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.9, 135.6, 134.3, 123.2, 28.3, 21.8. GC-MS (EI) *m/z*: 343.



Formula: $C_7H_5Cl_2NO$

Mass: 189

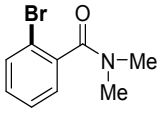
2,6-dichlorobenzamide (5h): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5h** as white solid (66.15mg, 70%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (s, 1H), 7.77 (s, 1H), 7.46 – 7.43 (m, 2H), 7.36 (dd, *J* = 8.9, 7.3 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 164.8, 136.5, 130.2, 130.1, 127.5. GC-MS (EI) *m/z*: 189.



Formula: C_7H_6BrNO

Mass: 199

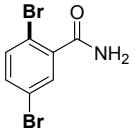
3-bromobenzamide ($3a_0$): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **$3a_0$** as white solid (82.59mg, 83%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.67 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 6.10 (s, 1H), 5.92 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.8, 135.9, 133.4, 130.0, 129.7, 126.0, 121.1. GC-MS (EI) *m/z*: 199.



Formula: $C_9H_{10}BrNO$

Mass: 227

2-bromo-N,N-dimethylbenzamide (3a'): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **3a'** as white solid (87.39mg, 77%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.36 (m, 1H), 7.27 – 7.22 (m, 2H), 3.14 (s, 3H), 2.86 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.3, 137.9, 133.0, 131.7, 129.2, 126.7, 118.2, 37.2, 33.7. GC-MS (EI) *m/z*: 227.

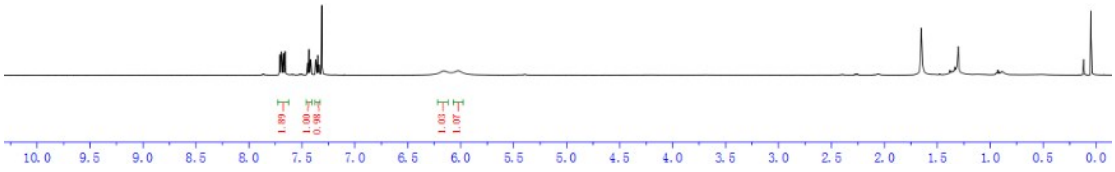


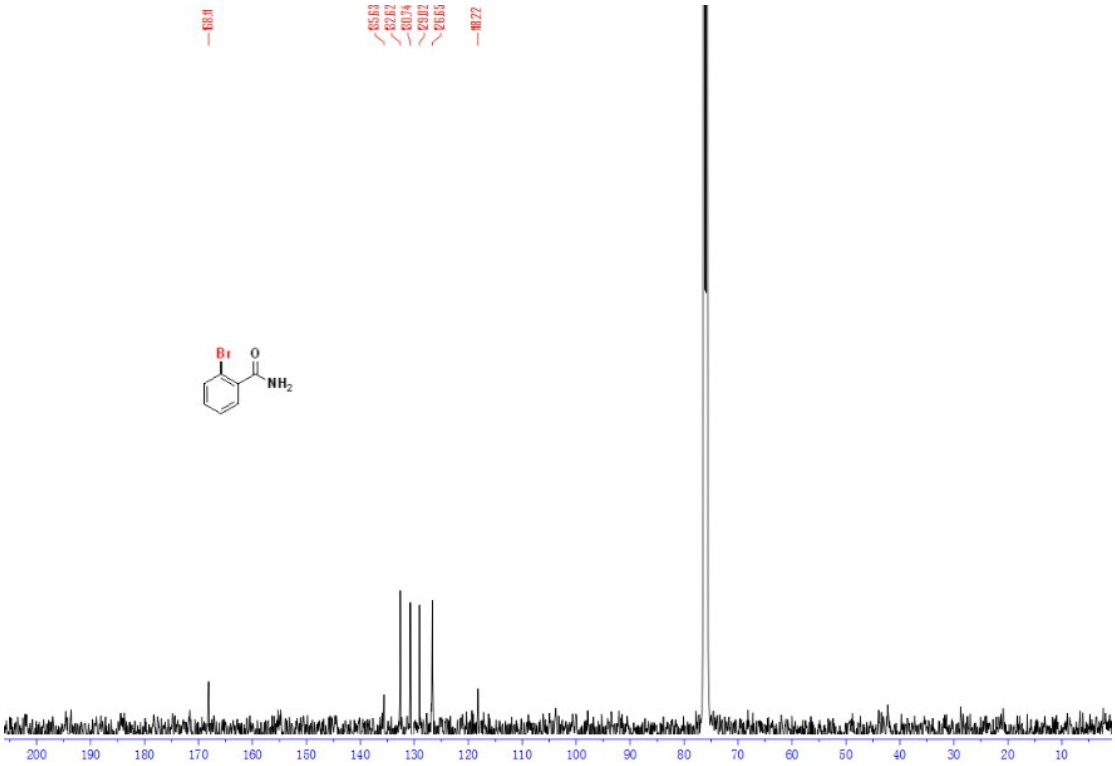
Formula: $C_7H_5Br_2NO$

Mass: 279

2,5-dibromobenzamide ($3a_0$'): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **$3a_0$'** as white solid (99.05mg, 71%).^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99 (s, 1H), 7.72 (s, 1H), 7.54 – 7.52 (m, 2H), 7.51 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.9, 143.9, 136.8, 136.6, 135.6, 133.7, 133.5. GC-MS (EI) *m/z*: 279.

4. NMR spectra



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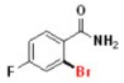
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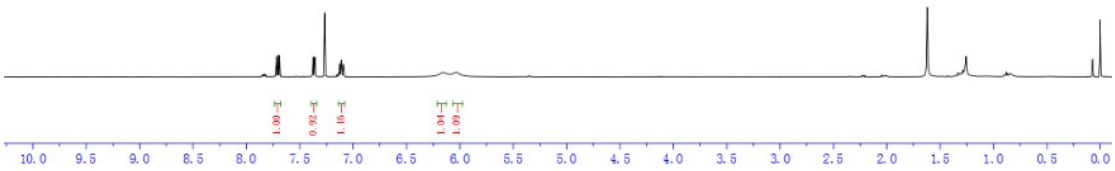
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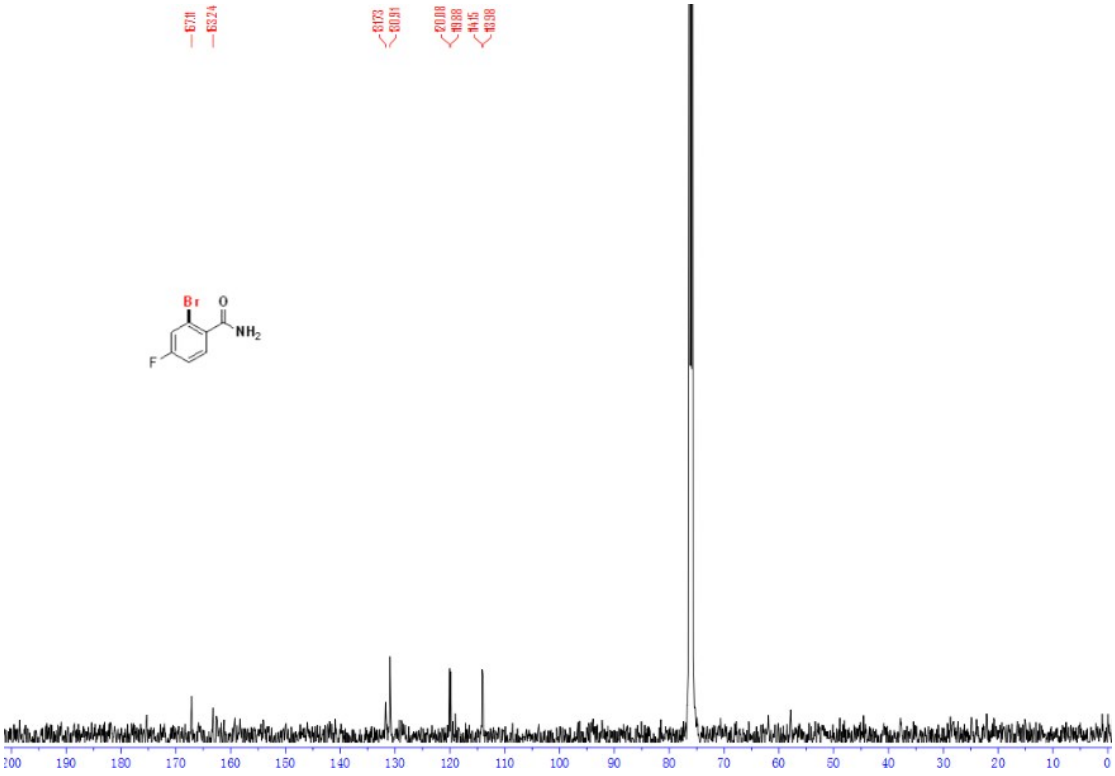
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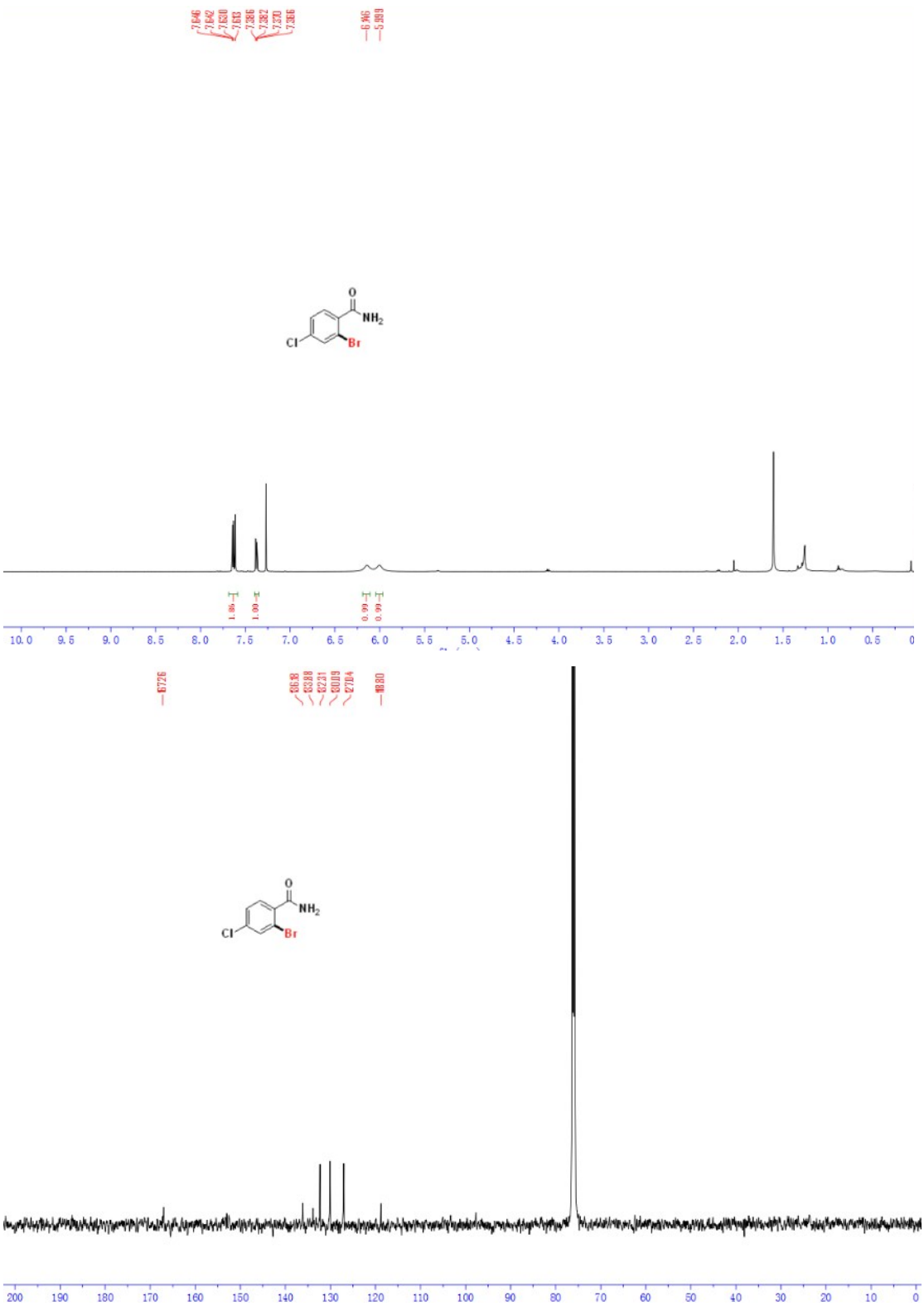
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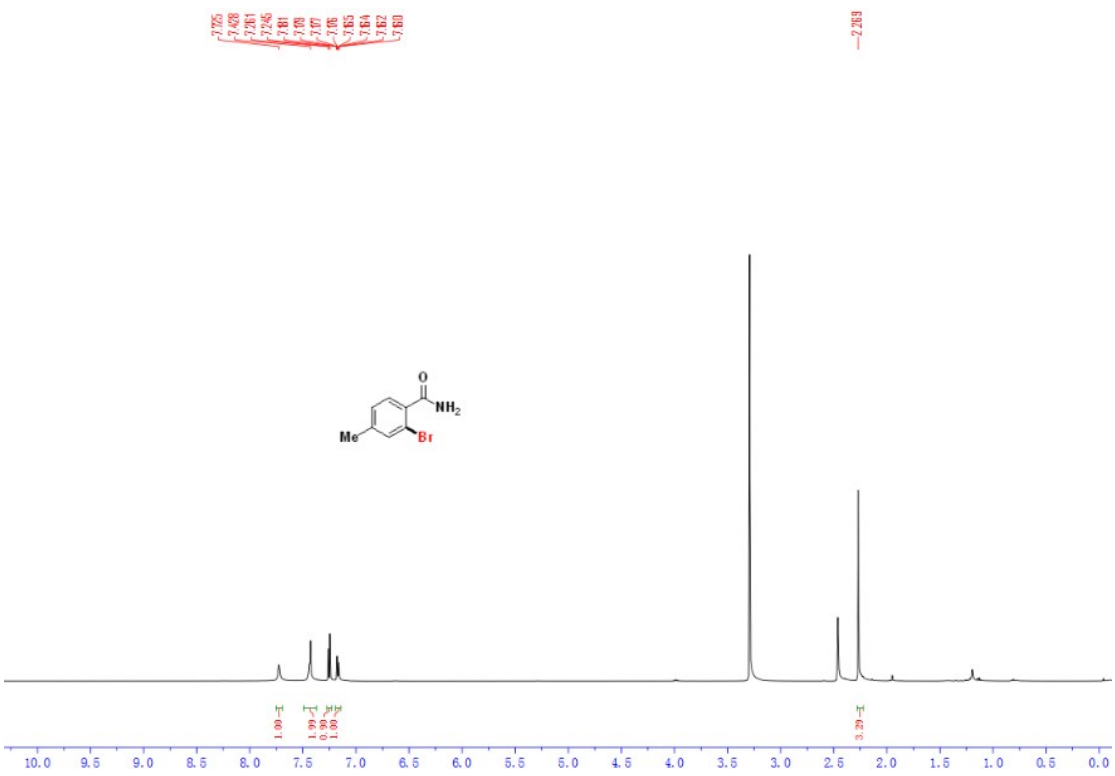
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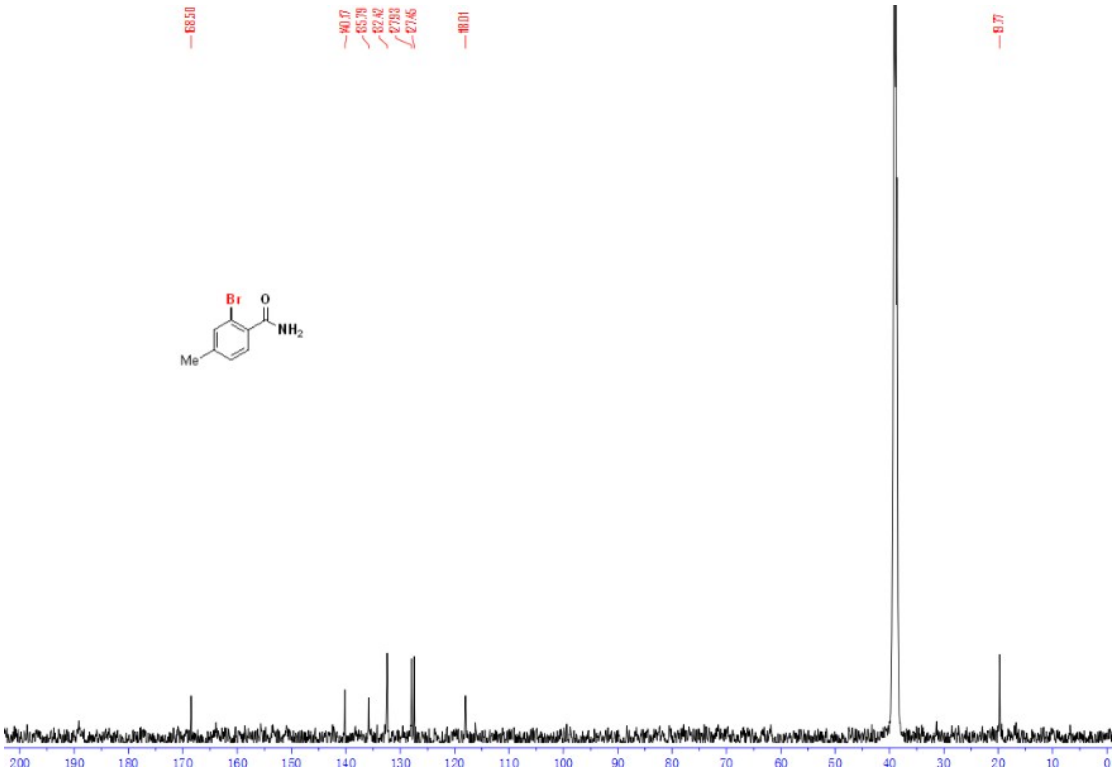
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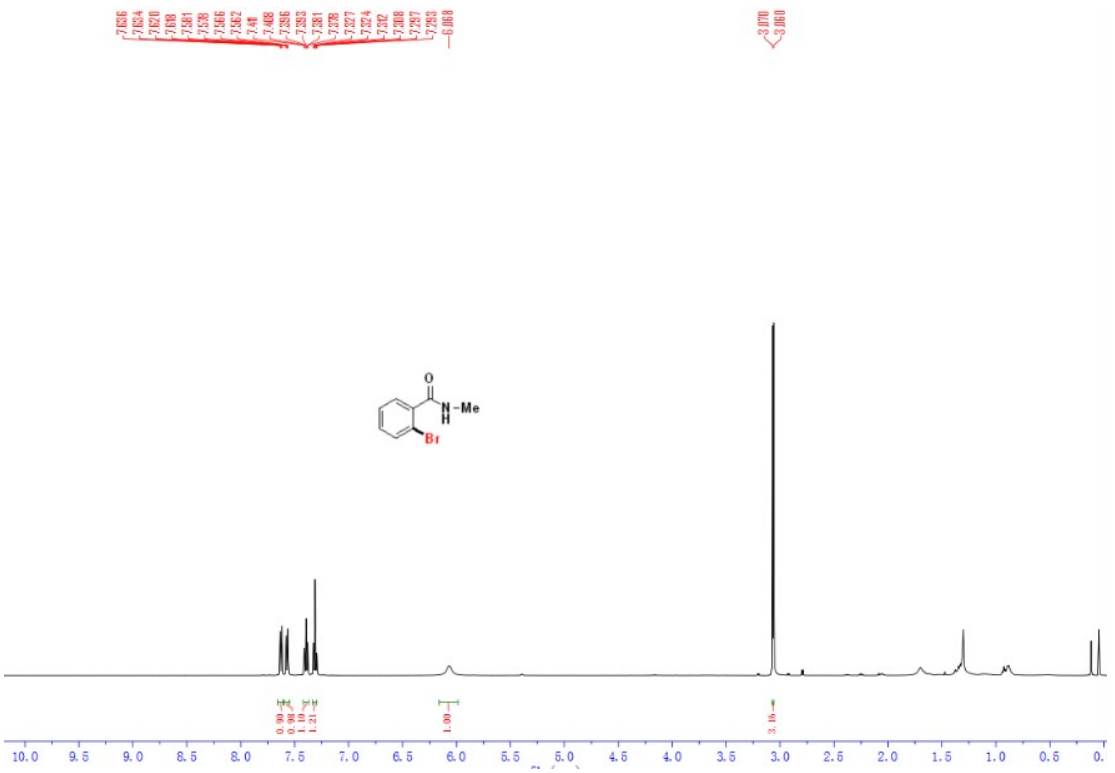
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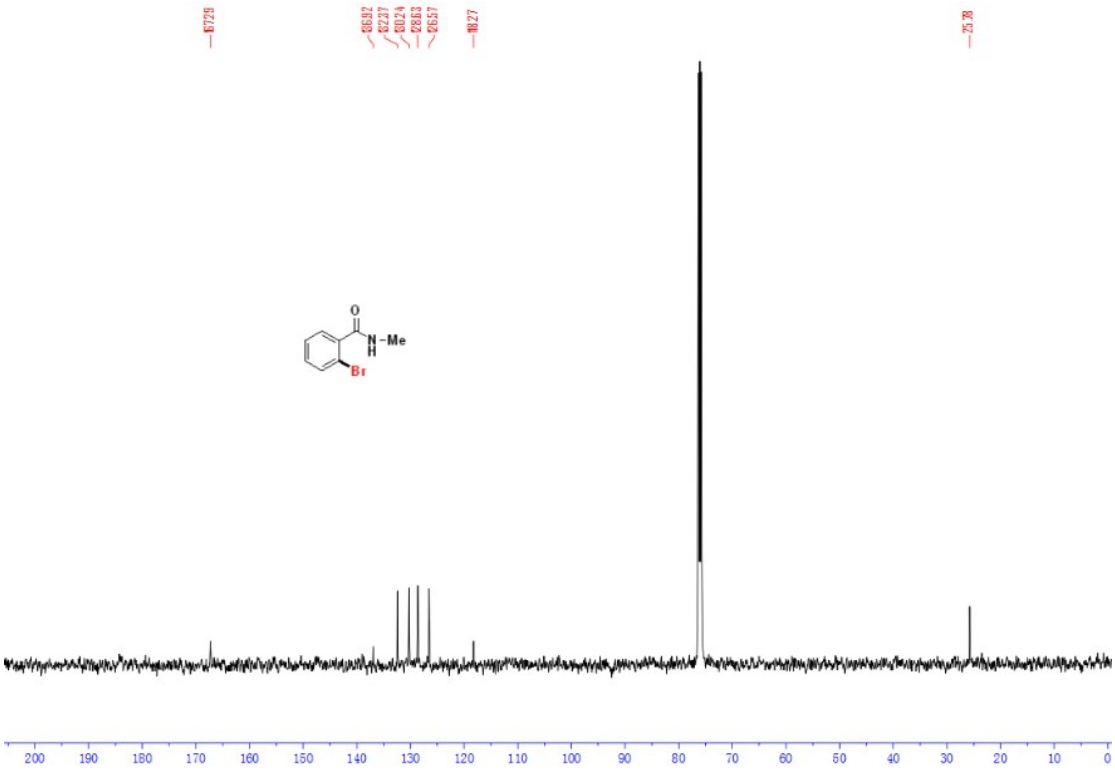
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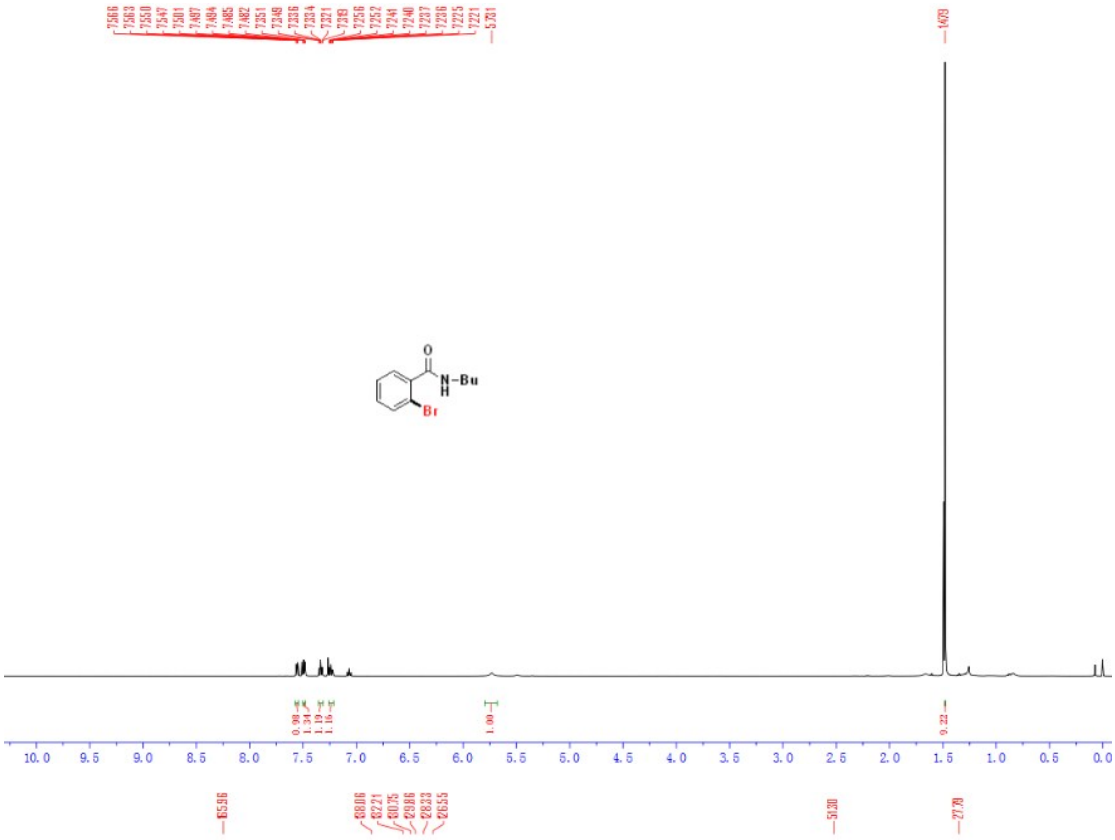
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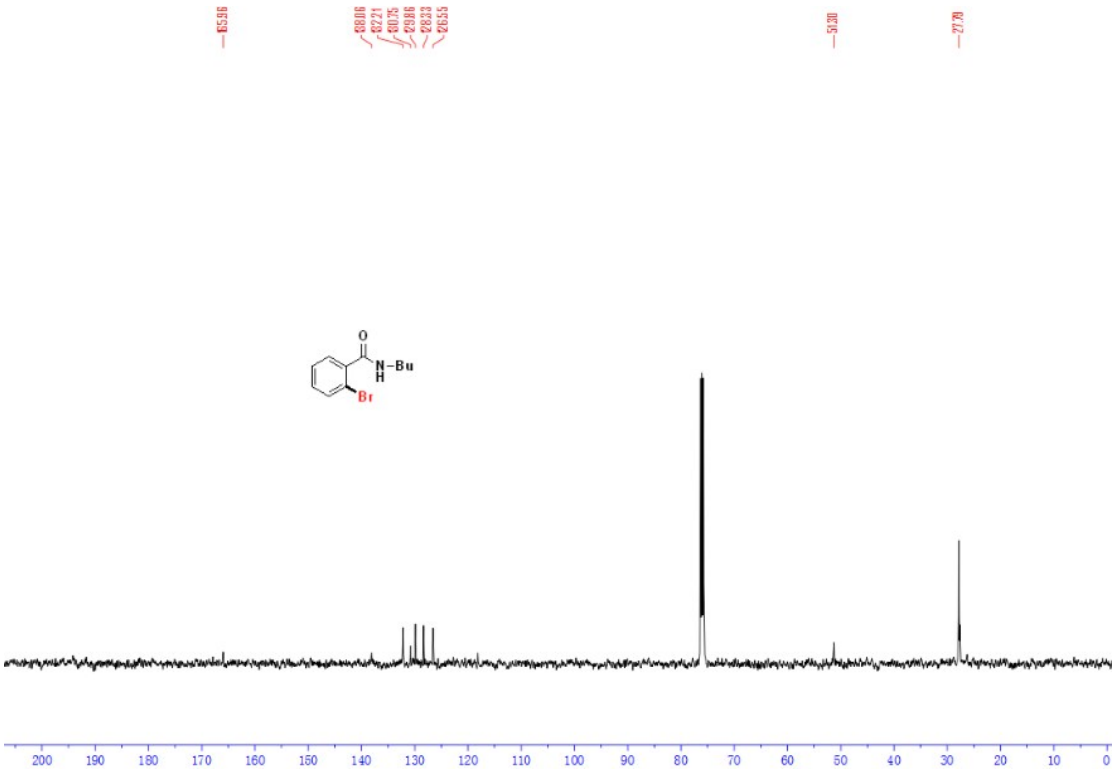
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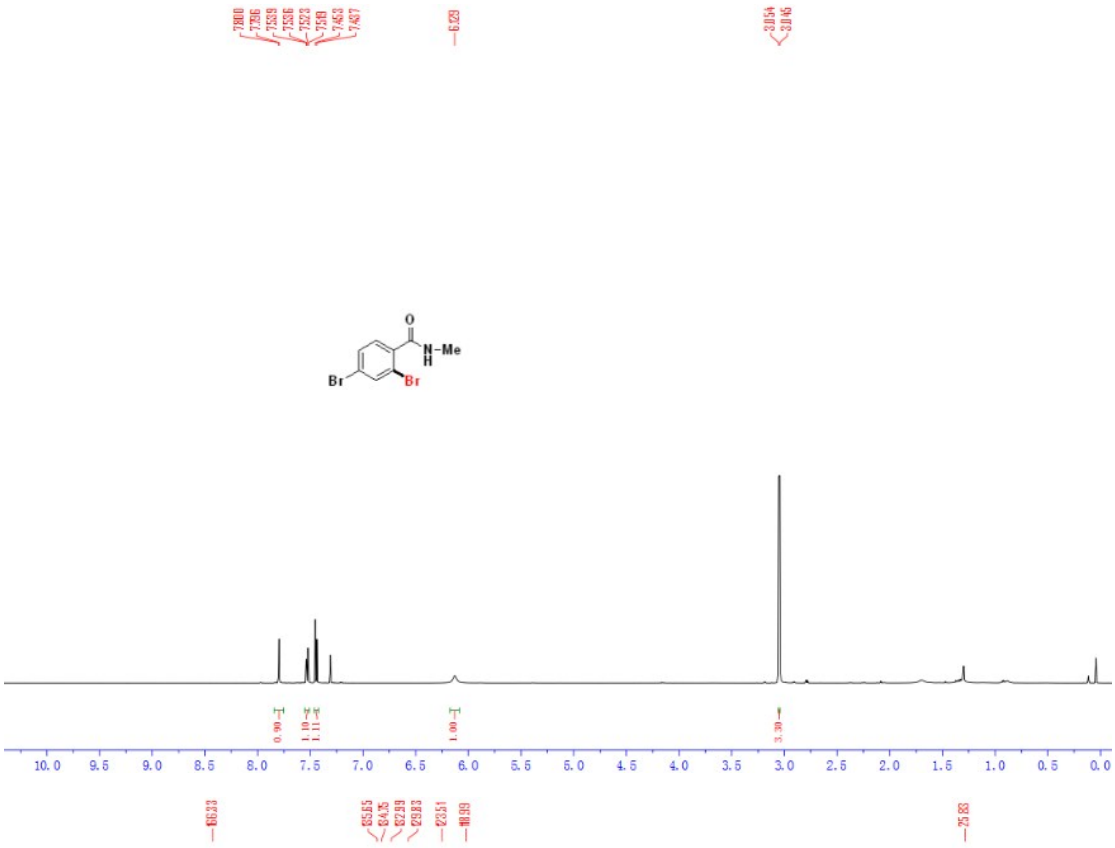
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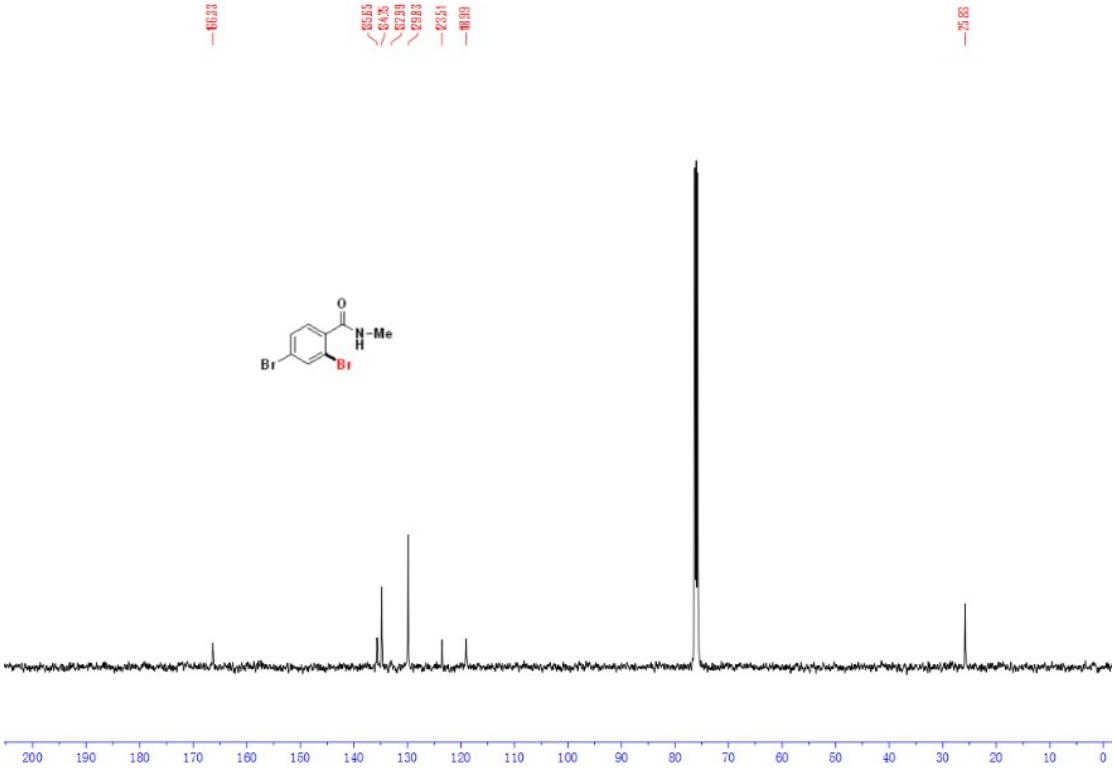
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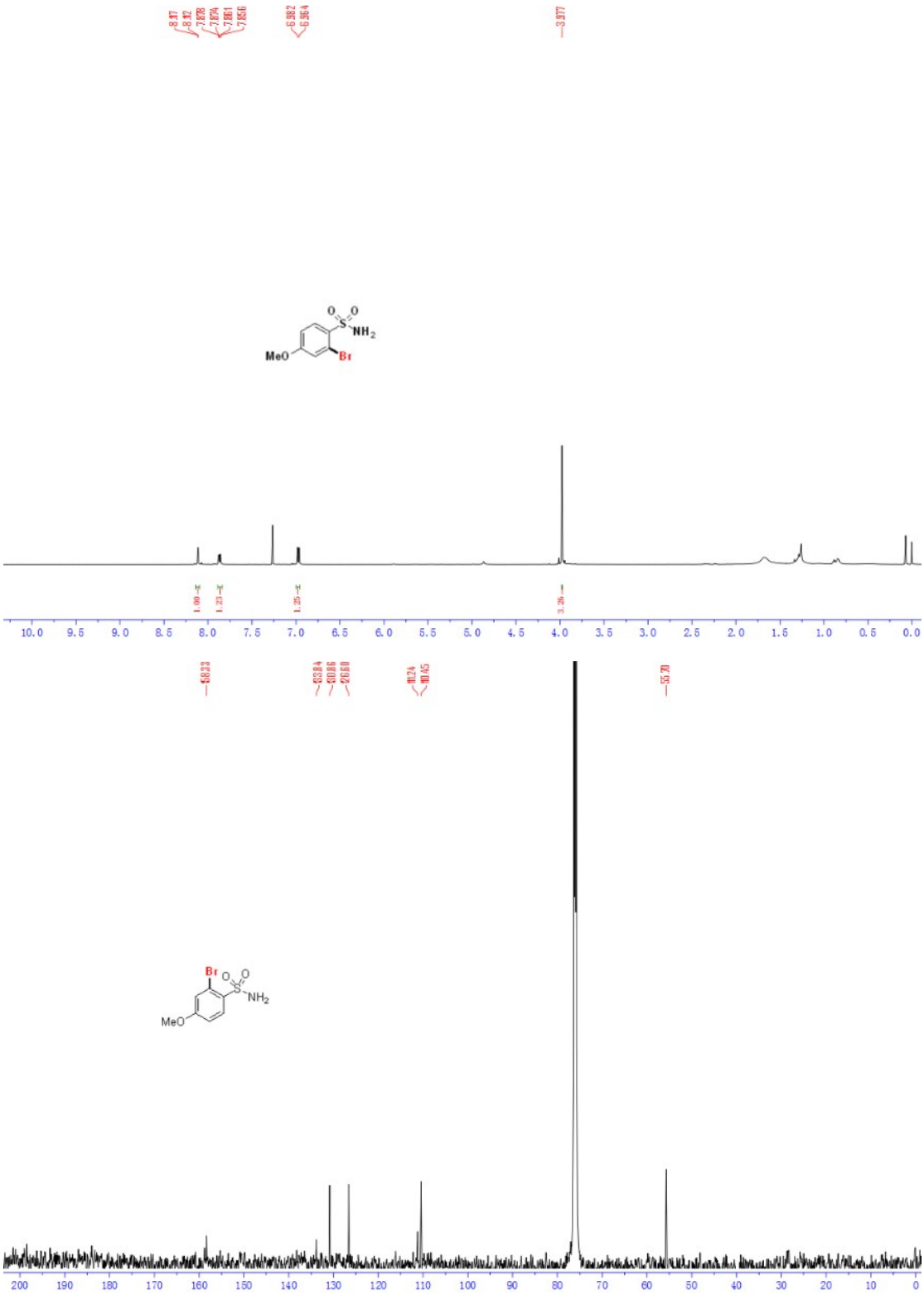
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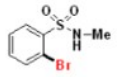
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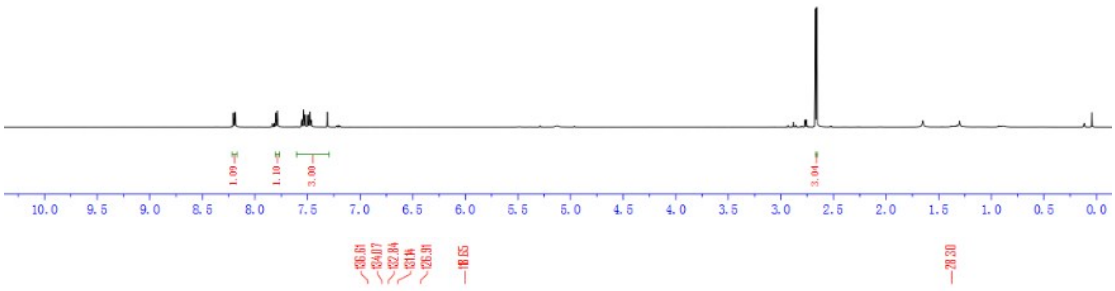
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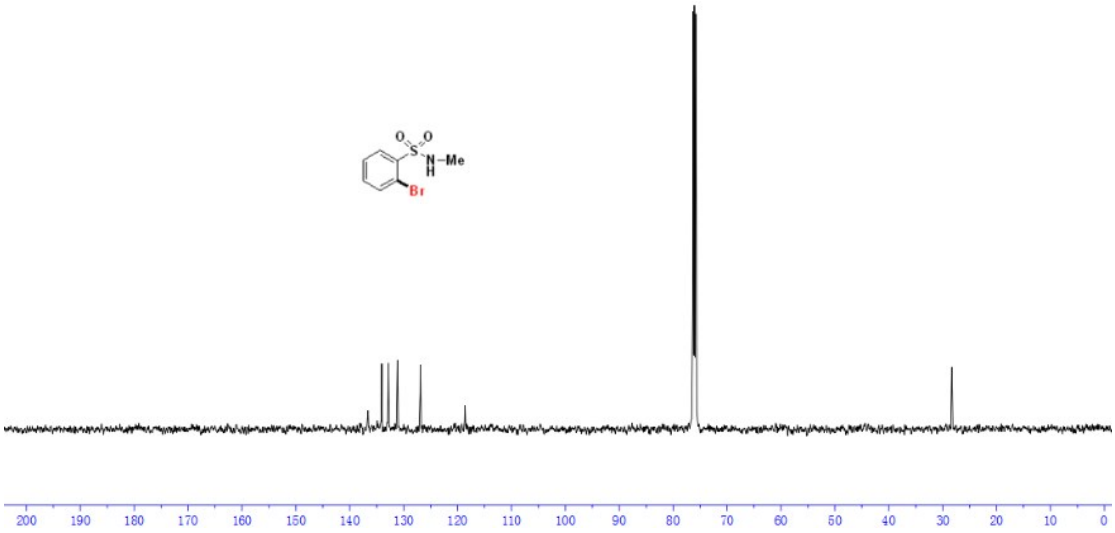
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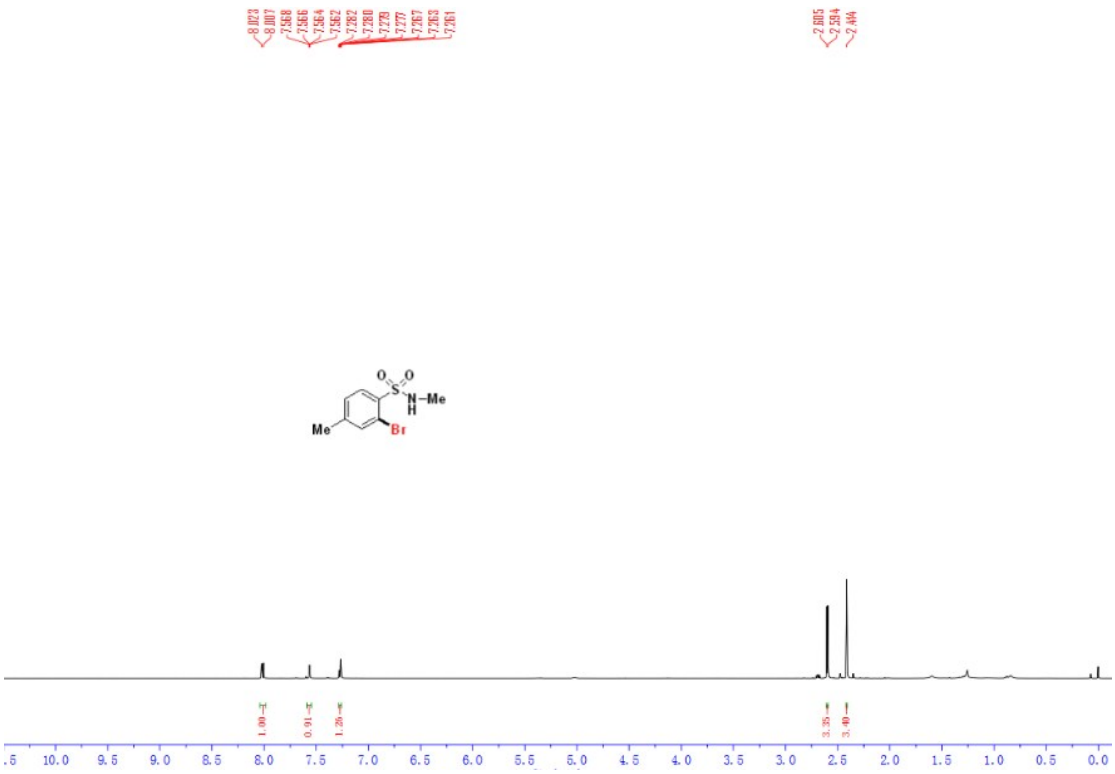
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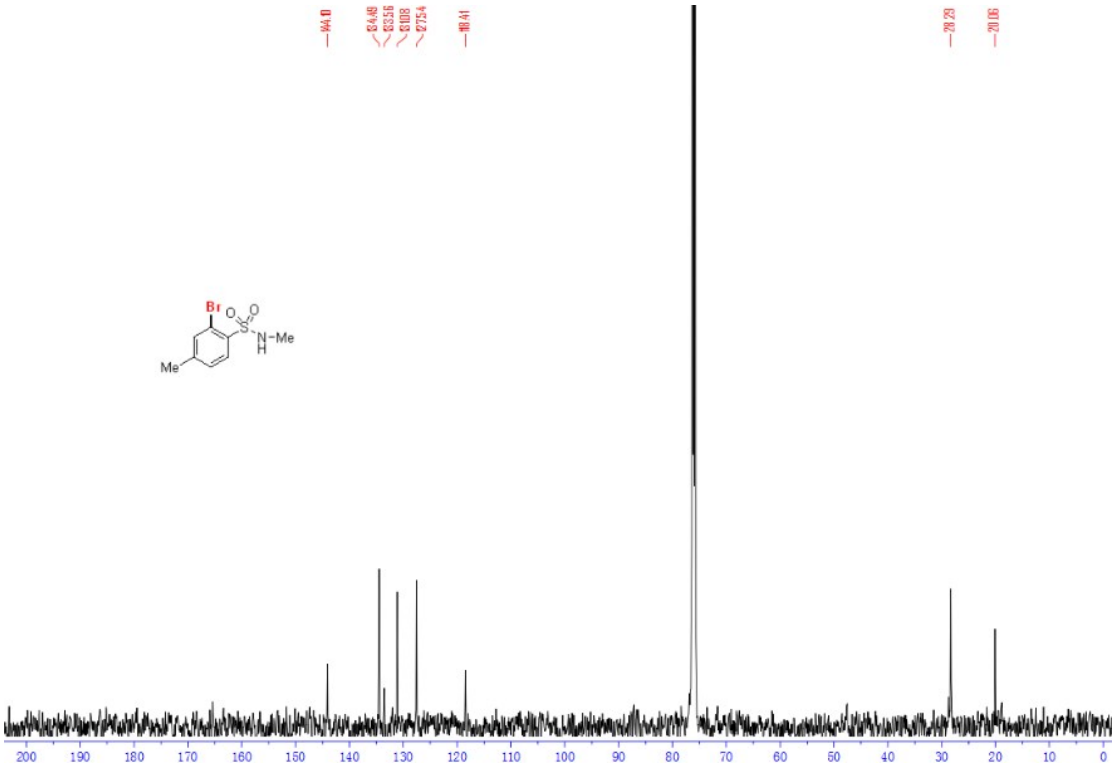
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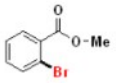
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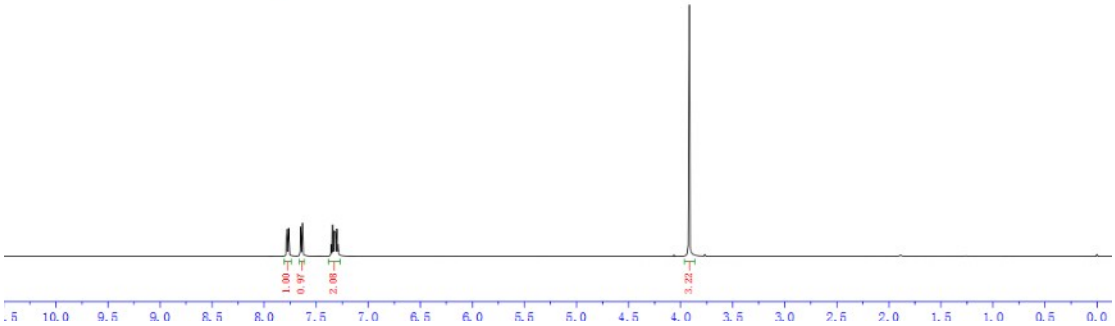
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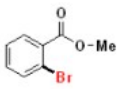
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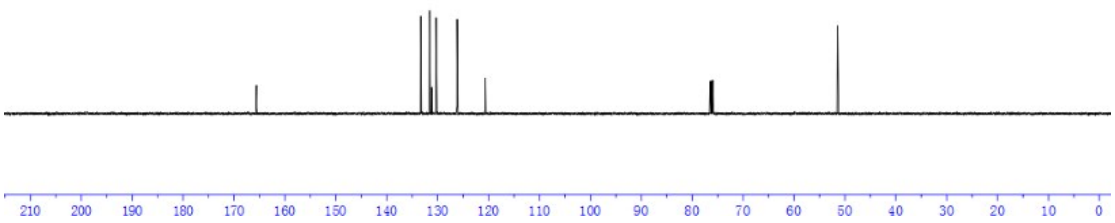
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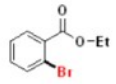

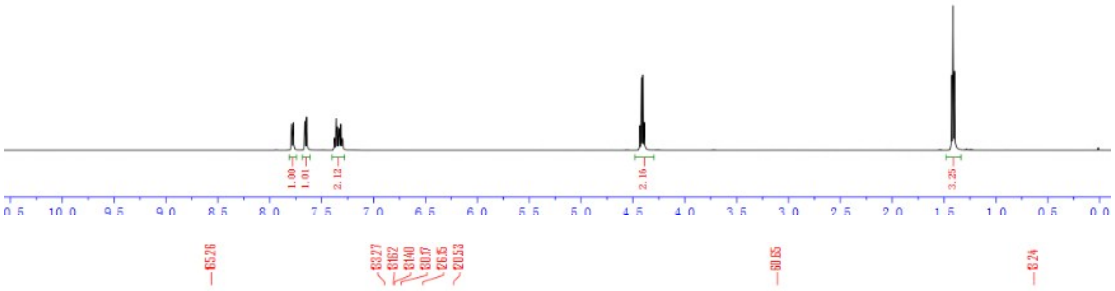

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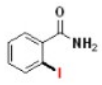

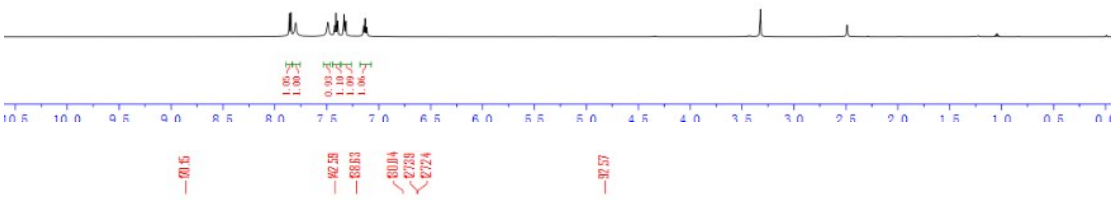

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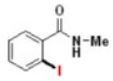

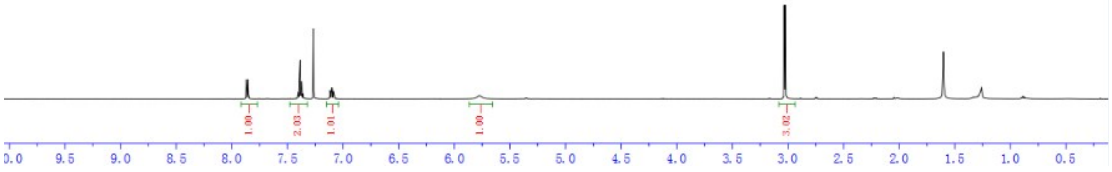

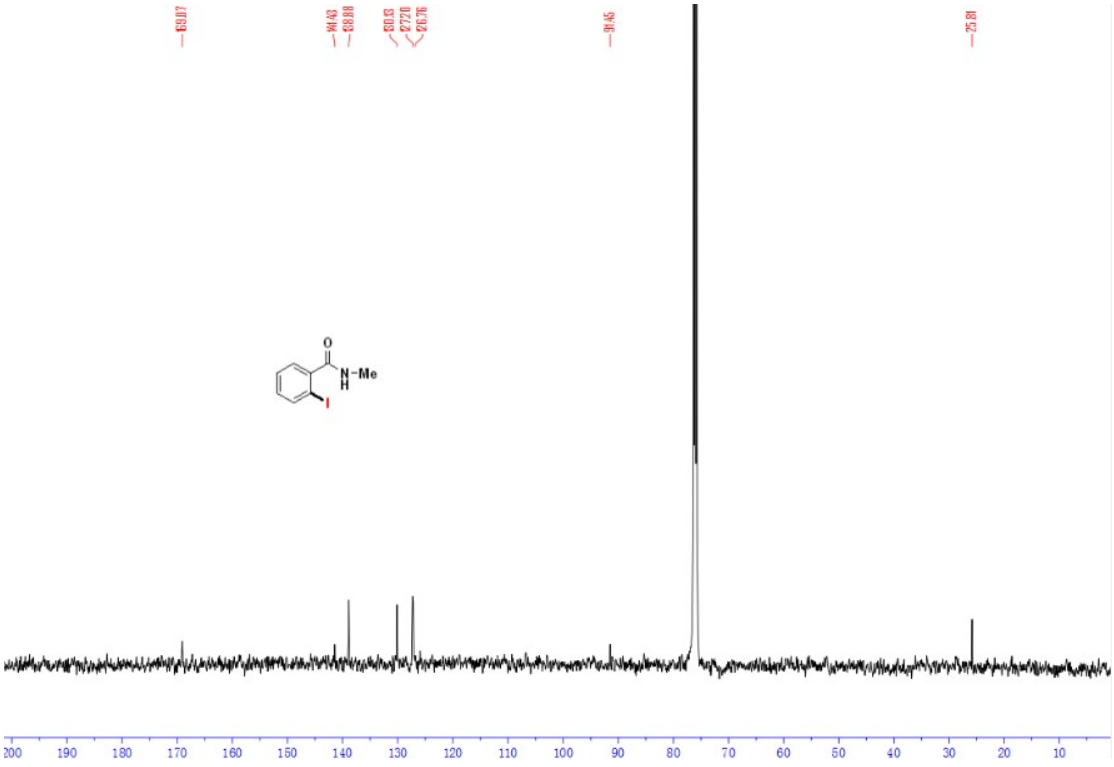

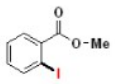

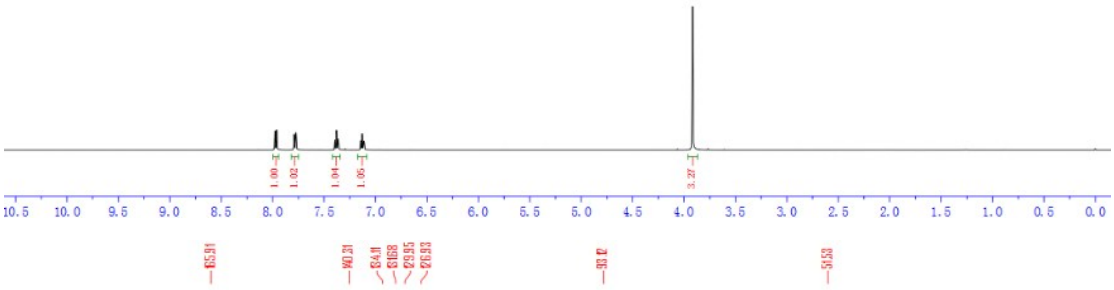

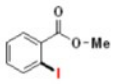

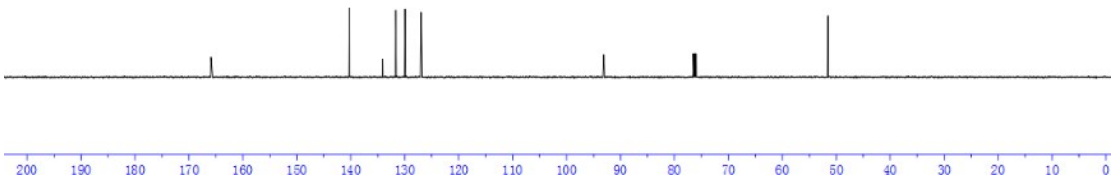

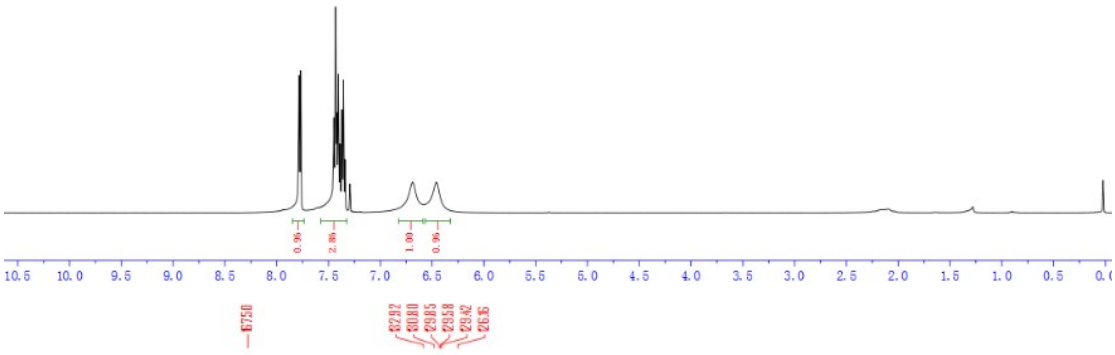

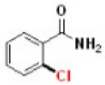

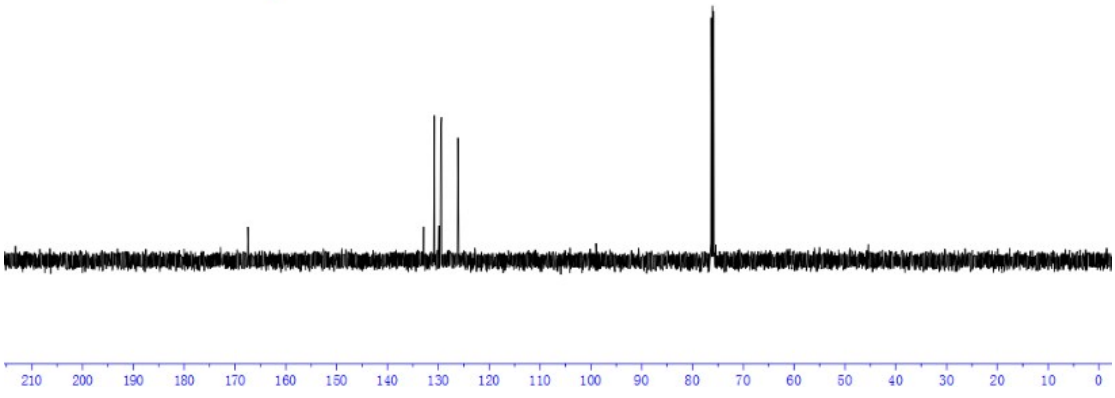

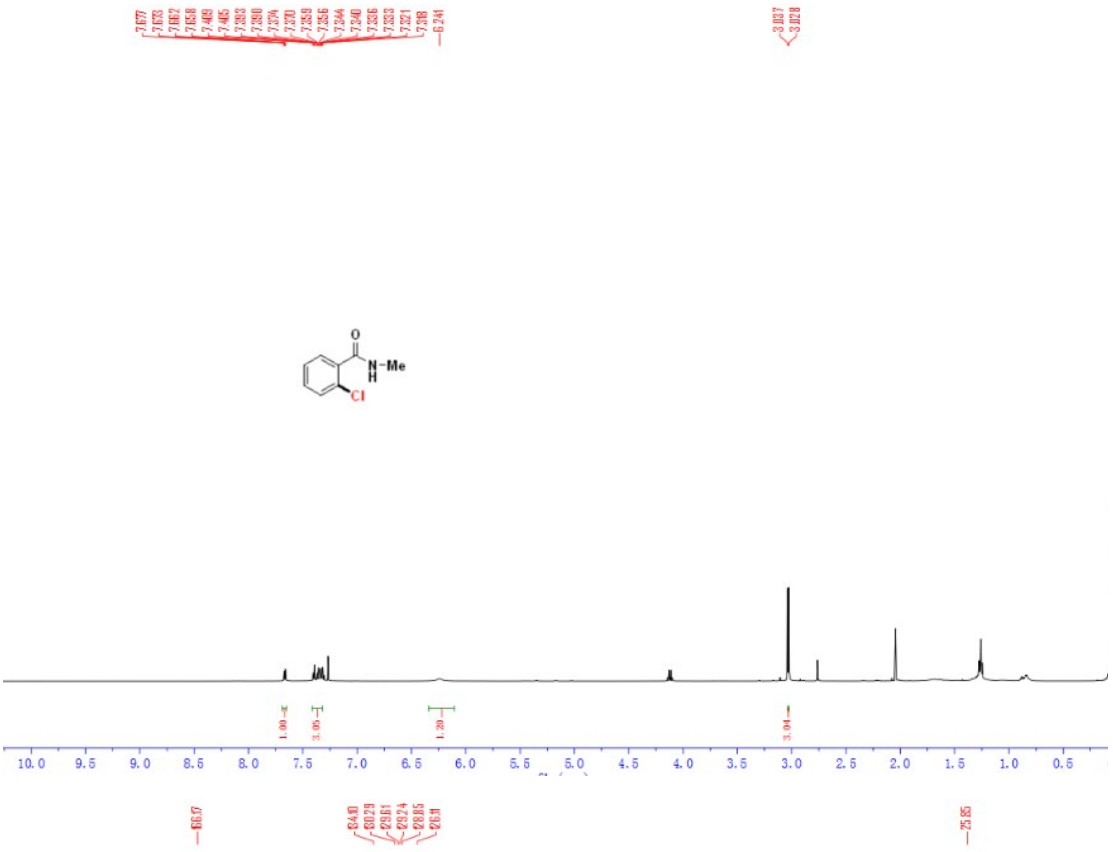
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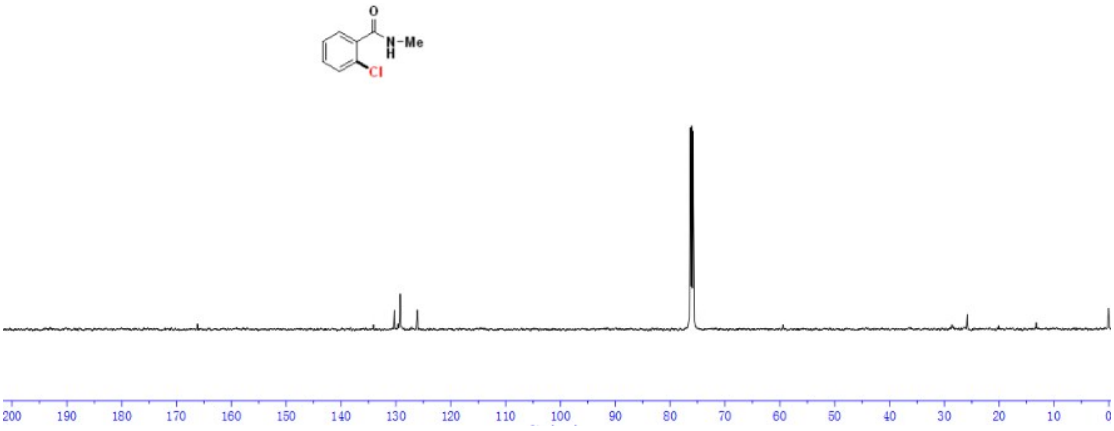
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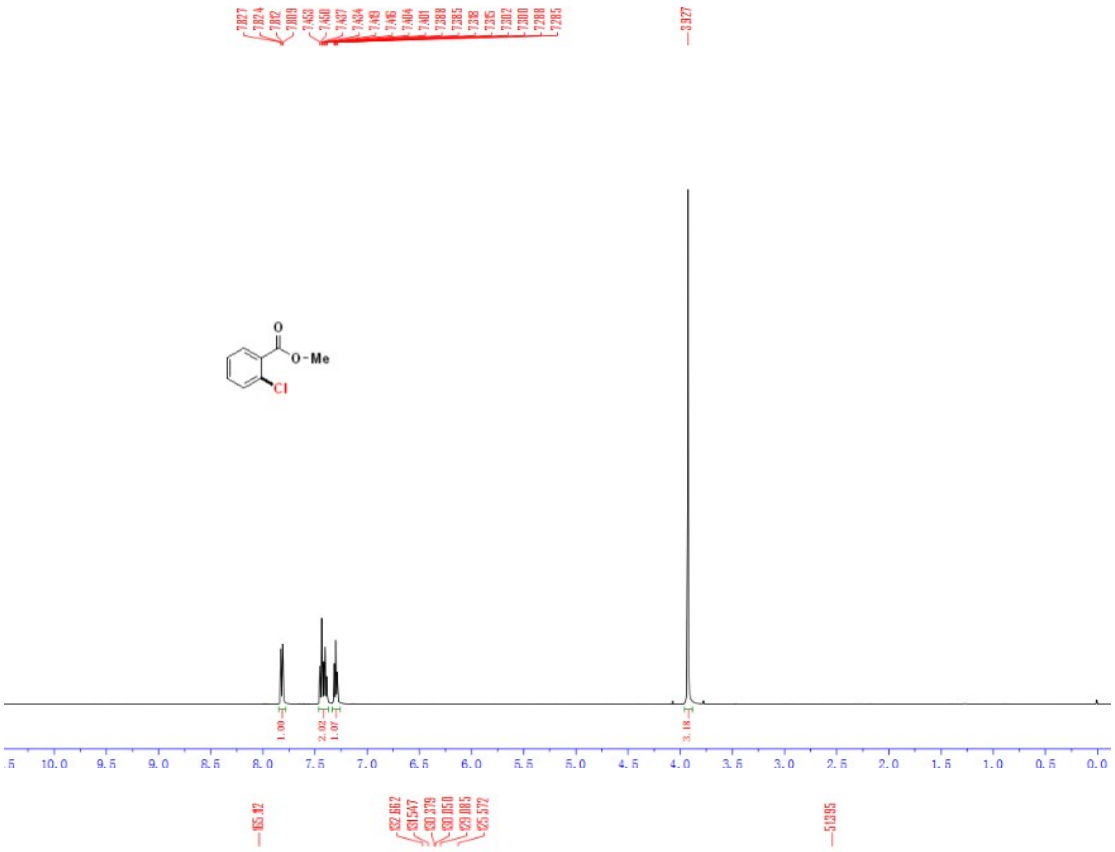
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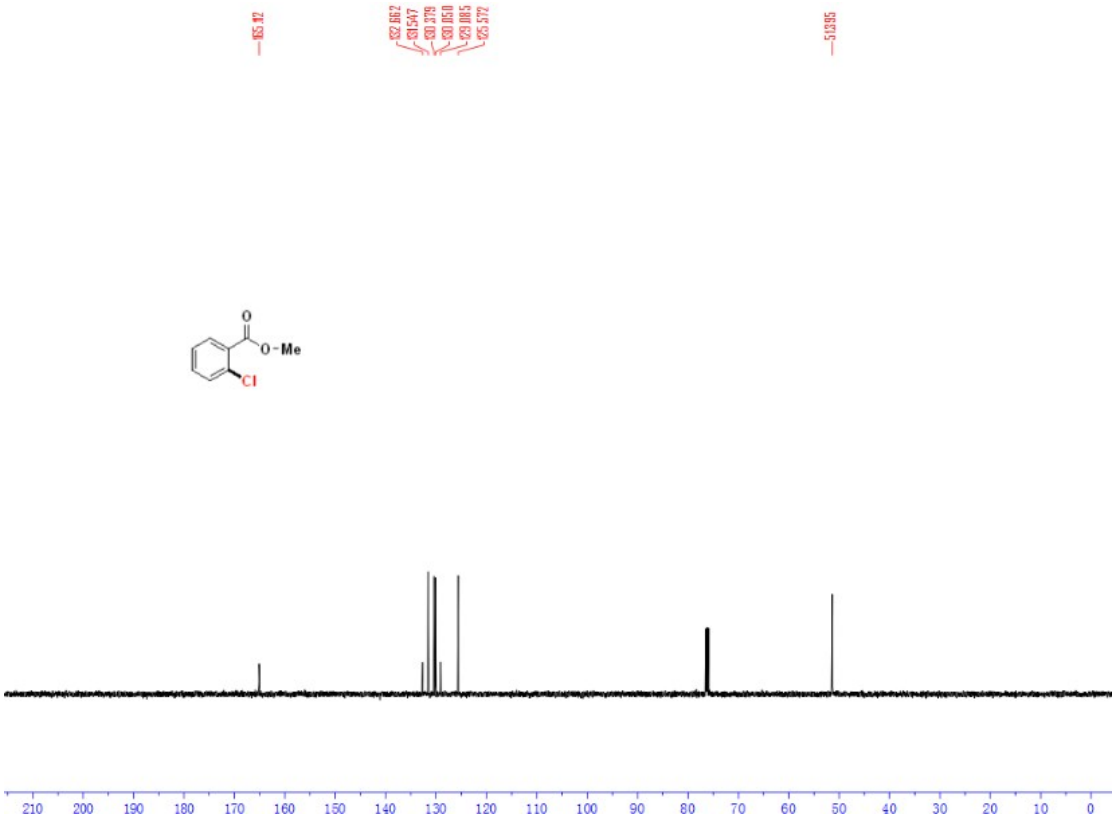
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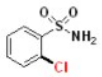

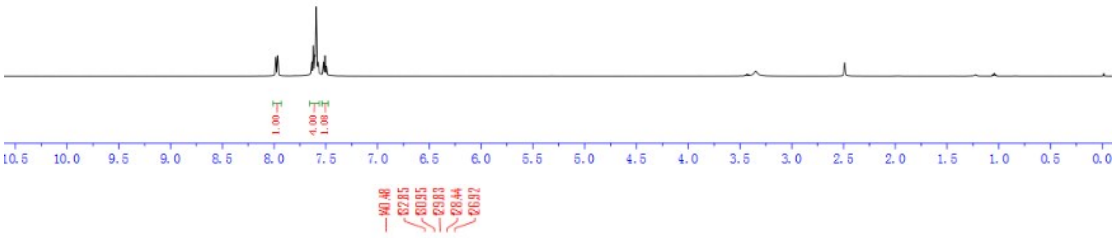

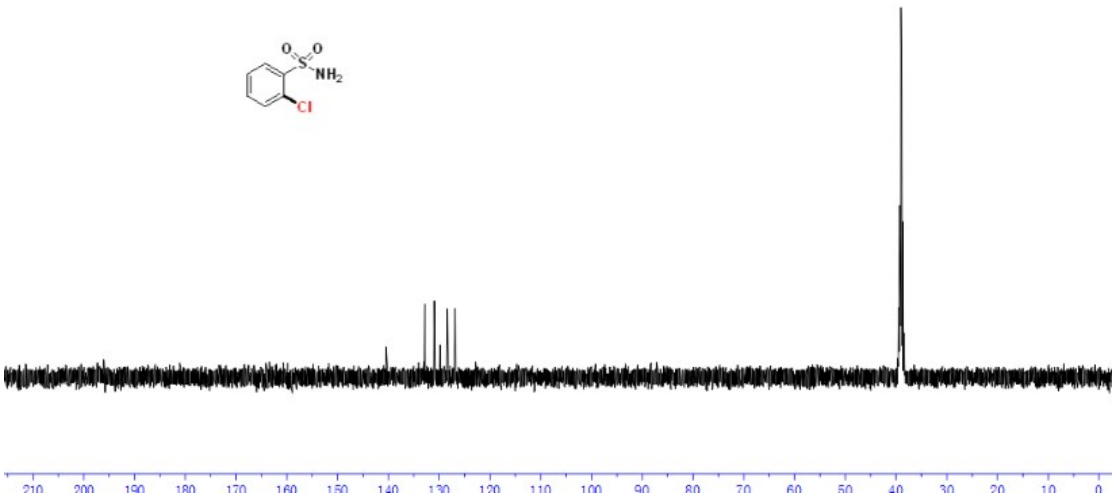

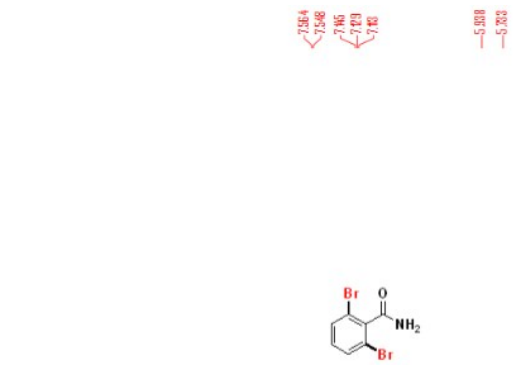
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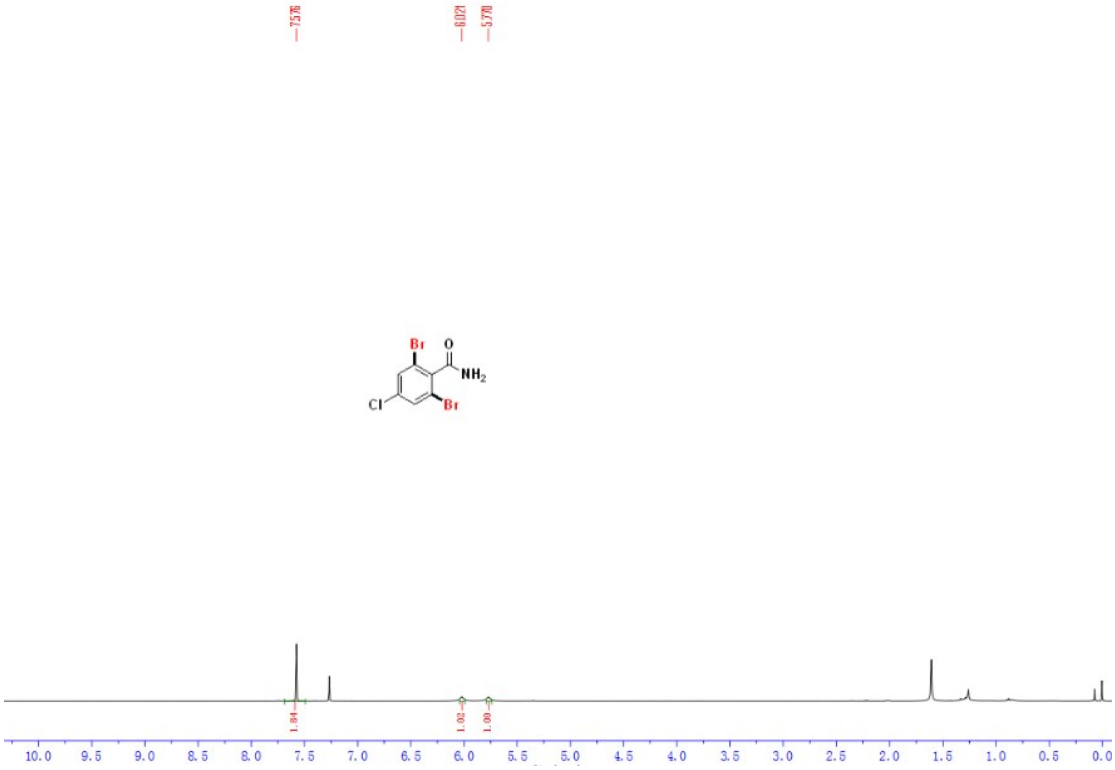
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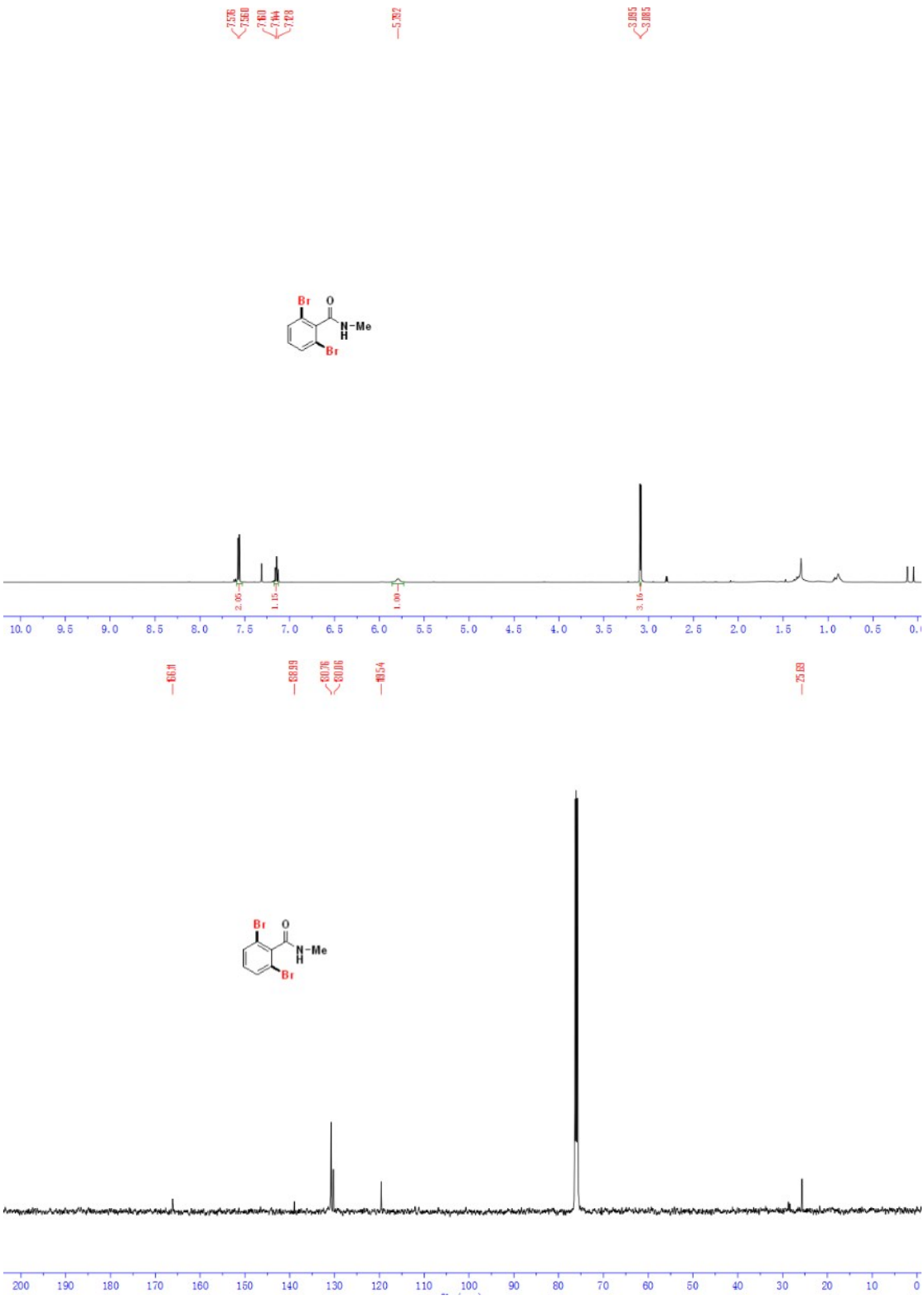
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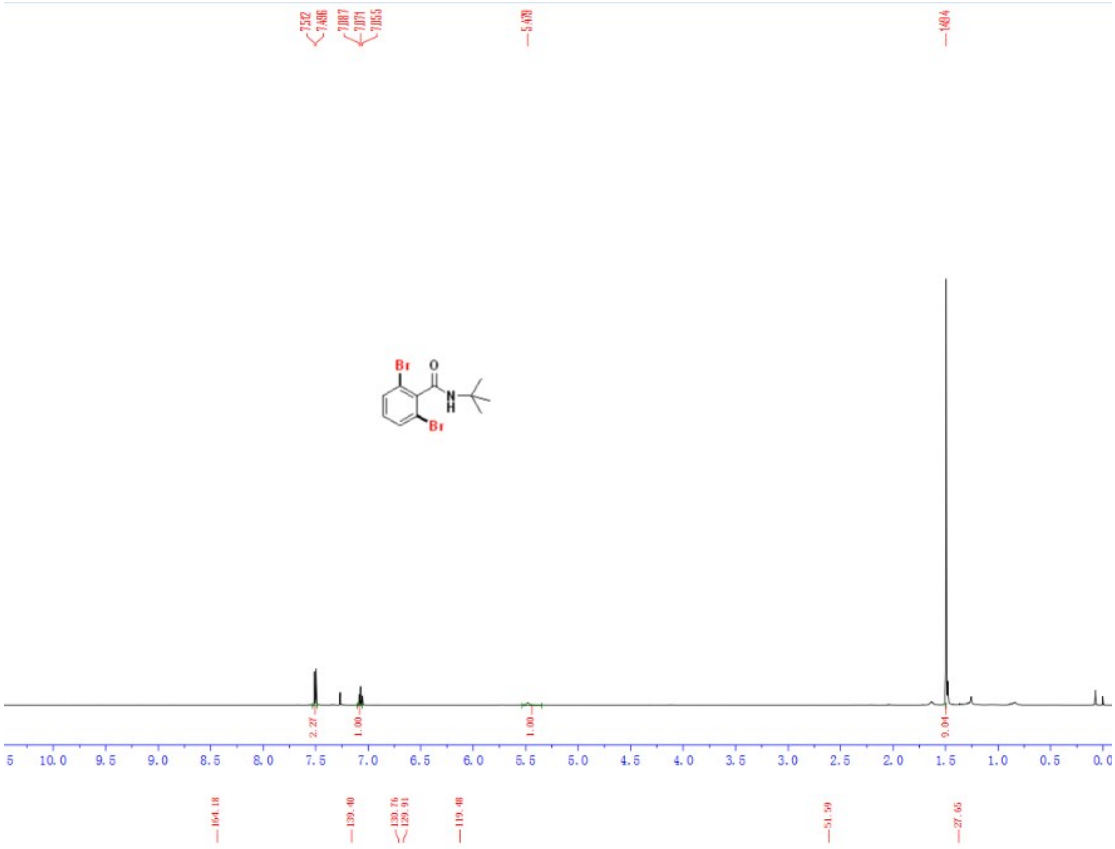
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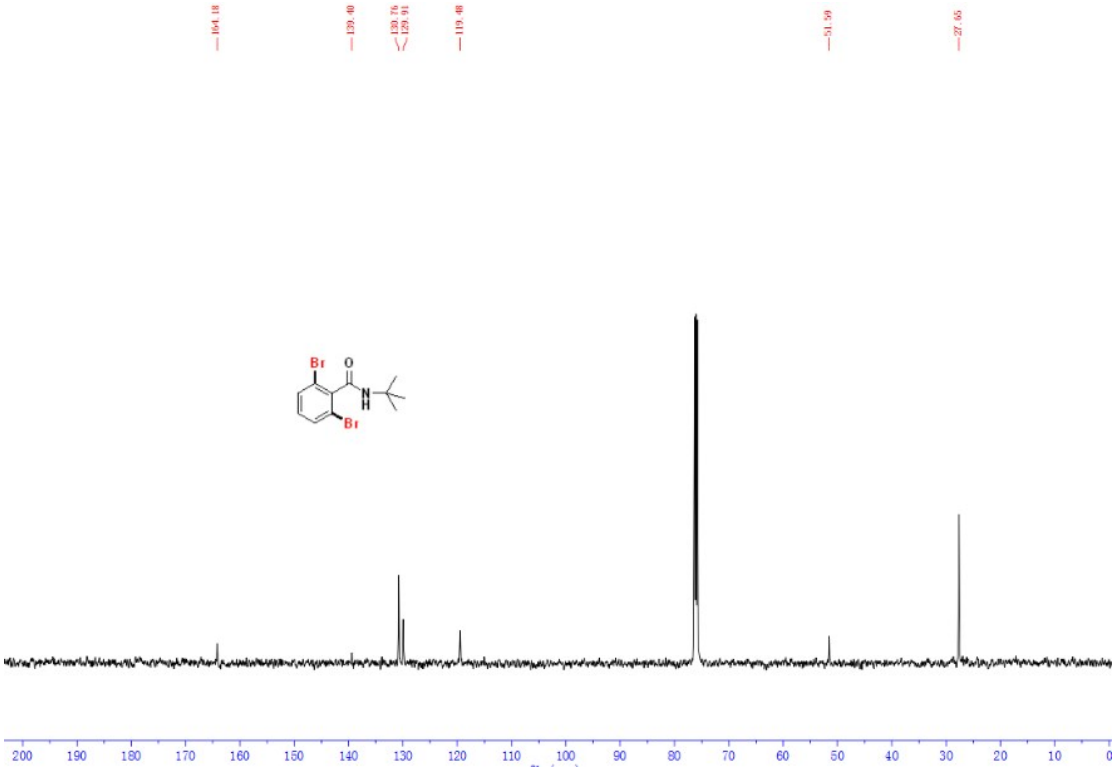
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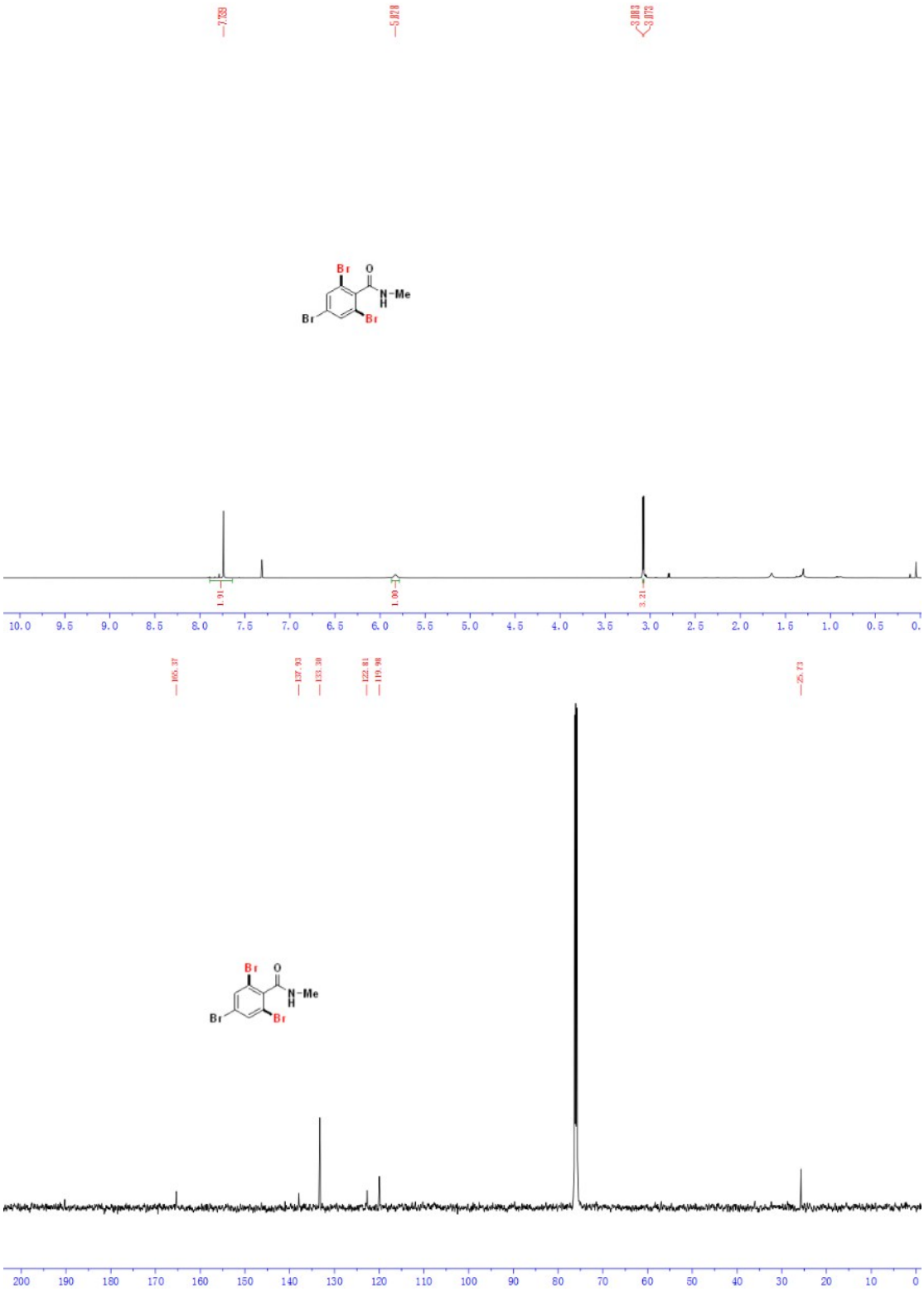
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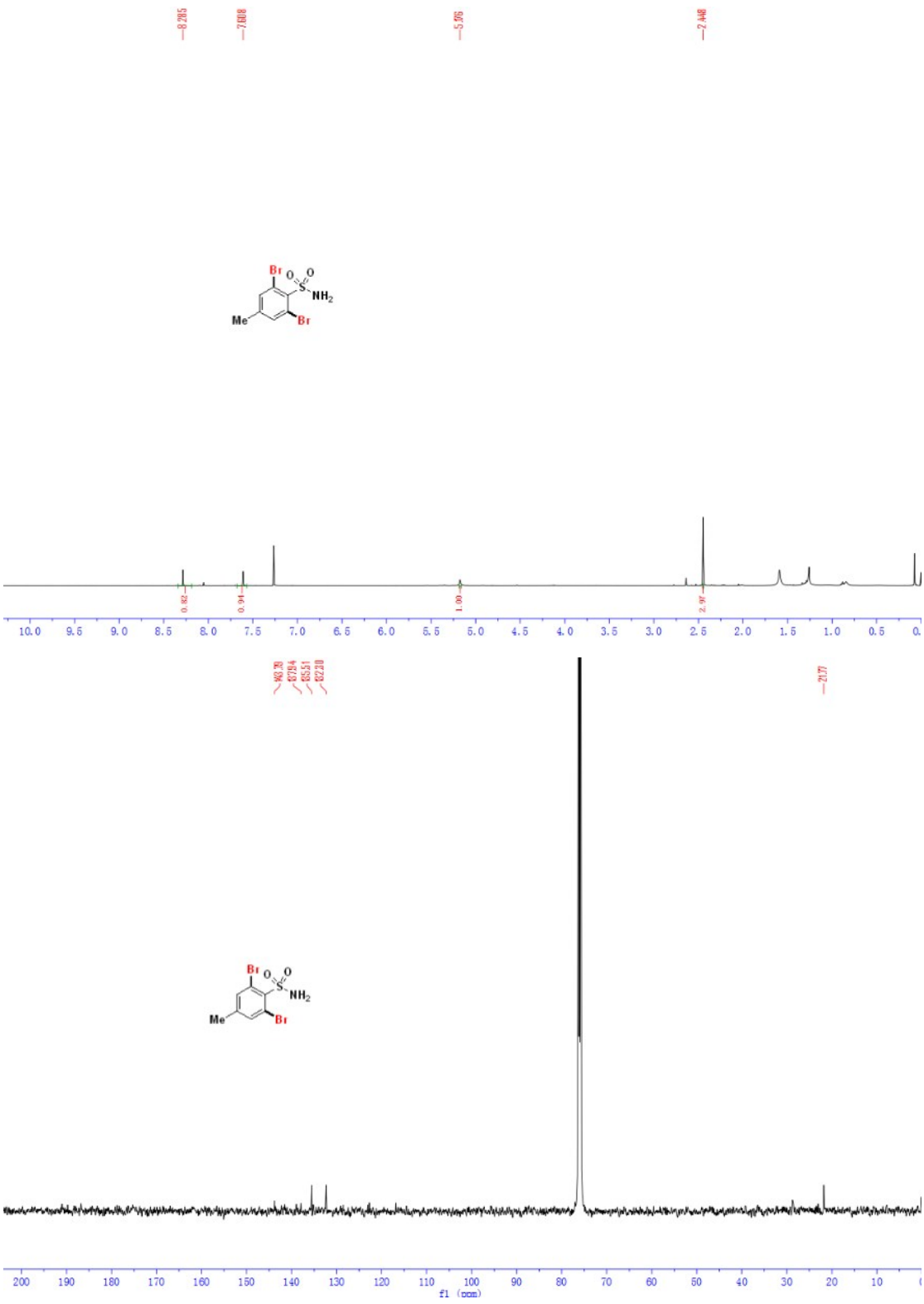
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2.448
Br
O
O
S
NH2
Me
Br
0.82
0.94
1.00
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
163.20
137.84
135.51
122.30
21.77
Br
O
O
S
NH2
Me
Br
200
190
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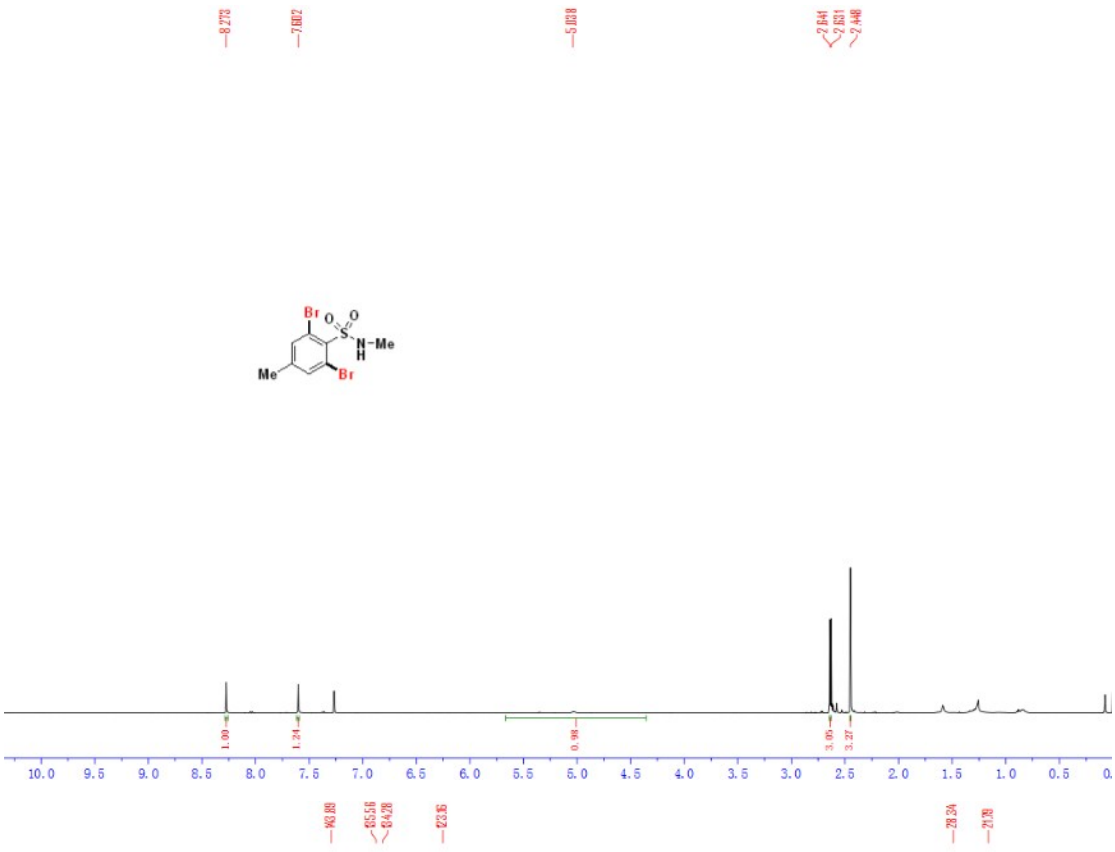
f1 (ppm)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O
S
N-Me
H
Me
Br
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1.24
0.98
3.05
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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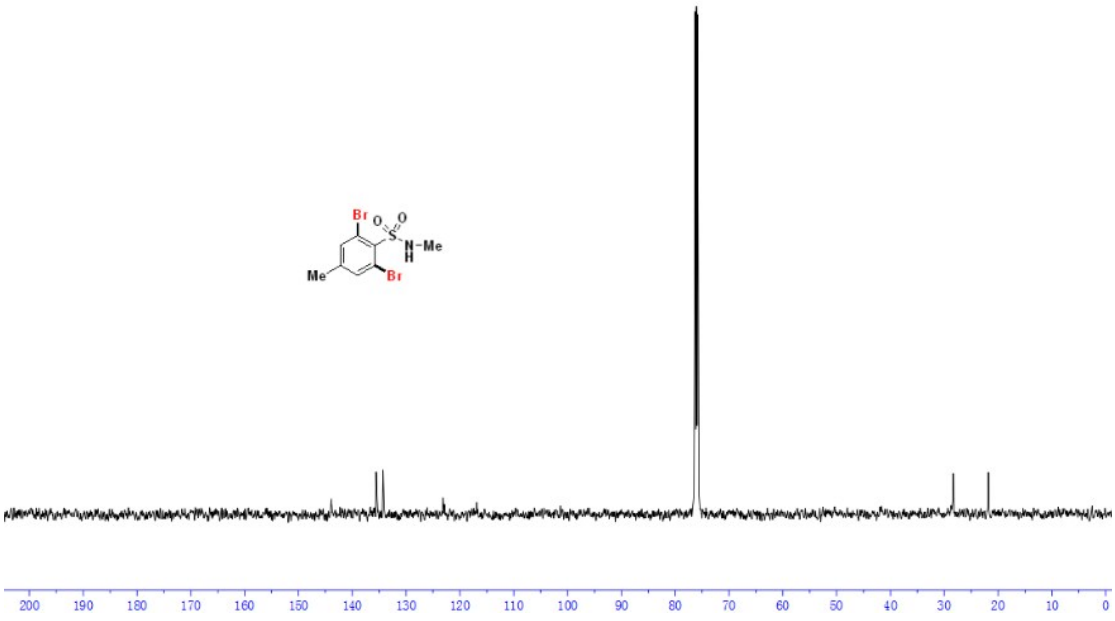
27.78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O
S
N-Me
H
Me
Br
200
190
180
170
160
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120
110
100
90
80
70
60
50
40
30
20
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7.7451
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7.7377
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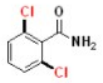
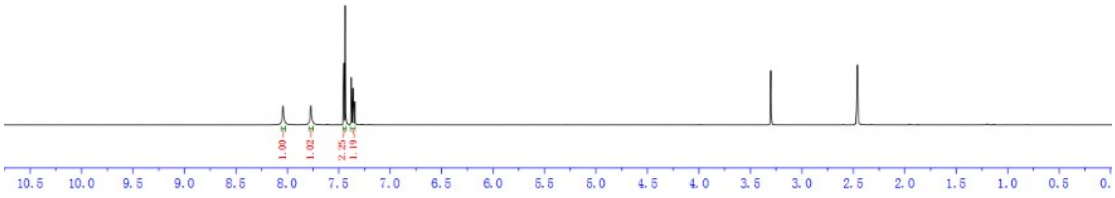
7.7353
7.7346


Cl
O
NH2
Cl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1.02
2.25
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9.0
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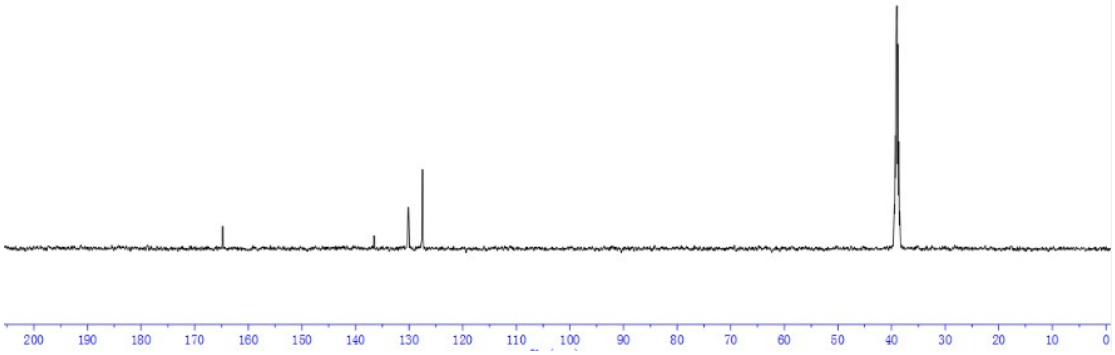
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.


164.78
136.51
130.16
130.08
127.52


Cl
O
NH2
Cl


200
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180
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150
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100
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70
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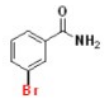
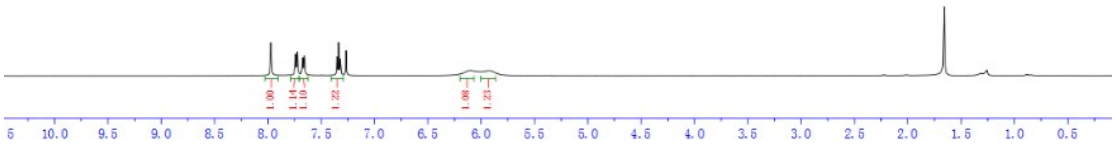
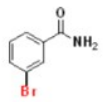
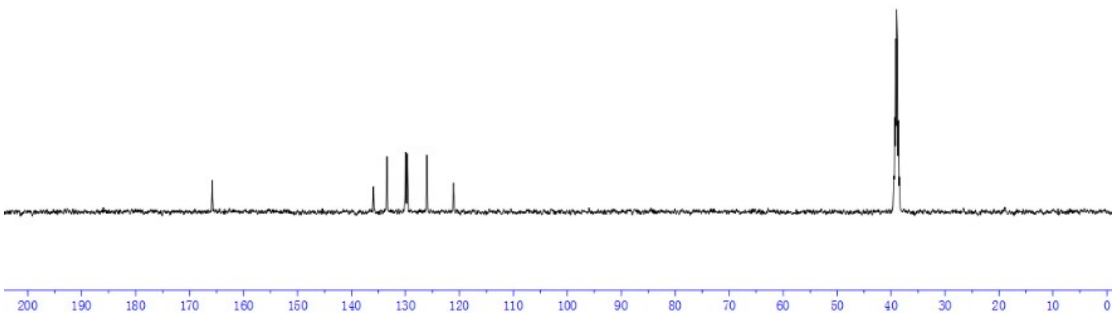
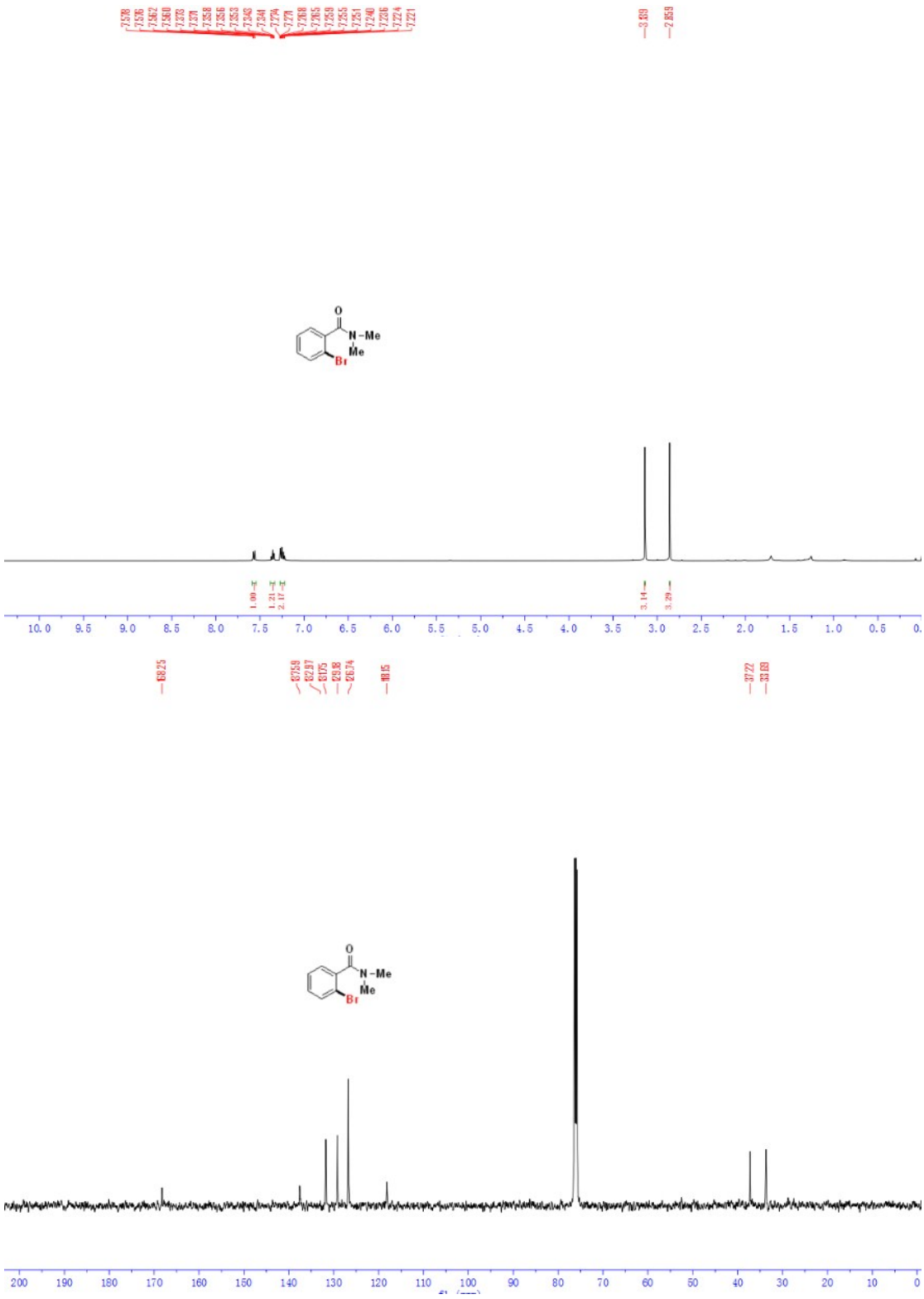
30
20
10
0







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7.269
7.265
7.259
7.255
7.251
7.240
7.236
7.224
7.221
3.459
2.859
O
N-Me
Me
Br
1.00
1.21
2.17
3.14
3.29
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7.5
7.0
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5.5
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4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
168.25
137.59
132.97
128.75
128.38
126.74
48.15
37.22
33.88
200
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
40
30
20
10
0


7.5883
7.5720
7.5537
7.5270
7.5193
7.5150
7.5052
Br
O
NH2
Br
1.00
1.01
2.06
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9.0
8.5
8.0
7.5
7.0
6.5
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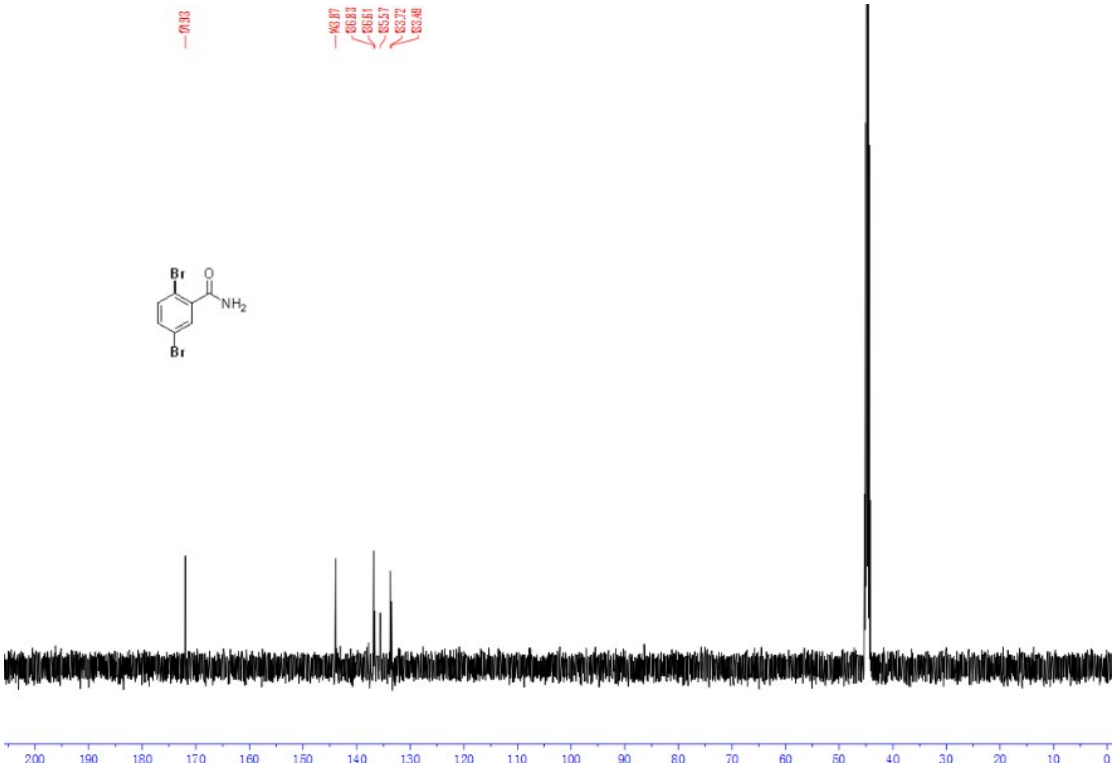
0.5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140.87
135.83
135.51
135.57
133.72
133.48
Br
O
NH2
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0